EFFECTS OF SINGLE AND MIXED ALKANES ON INTERFACIAL PROPERTIES, SOLUBILIZATION IN MICROEMULSIONS AND THE OIL DISPLACEMENT PROCESS

BY

FAISAL IBRAHIM ISKANDERANI

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by

Faisal Ibrahim Iskanderani

To
my mother, my brother Mahmoud
and my wife.

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By

Faisal Ibrahim Iskanderani

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The objective of this study is to provide a broad framework of understanding of the effect of single and mixed alkanes having the same equivalent alkane carbon number (EACN) on phenomena arising from the mixing of a surfactant, brine, oil and in some cases a cosurfactant, and from the use of a surfactant slug for tertiary oil recovery.

It was observed that the surfactant (0.2% TRS 10-80) lowers the interfacial tension between equilibrated brine and alkane or mixtures of alkanes of identical EACN to the same extent (within one order of magnitude).

Single and mixed alkanes of identical EACN, when used as the oil component in surfactant systems containing 5% TRS 10-410, 3% isobutanol, brine and oil, produce systems with the same phase and coalescence behavior. As the EACN of oil increases, the optimal salinity increases linearly, the solubilization parameter at optimal salinity decreases and the salinity range in which the system exhibits three phases increases. The molar ratio of alkanes in the middle phase microemulsion is the same as that in the excess oil phase.

Studies revealed that maximum oil recovery is obtained at the optimal salinity of the surfactant formulation. The desirable conditions for maximum oil recovery were found to be as follows: the surfactant/alcohol slug should form a system of ultralow interfacial tension, should have a wide range of three-phase salinity, a high solubilization capacity and a rapid separation of the macroemulsion into three phases, and should consist of an alcohol with relatively low partitioning in brine or oil. Results also reveal that the EACN concept is valid for oil displacement studies in porous media.

It is shown that the Schulman-Bowcott titration curve to obtain a clear microemulsion of a sodium dodecyl sulfate, n-Hexanol, water and alkane system goes through a minimum at a specific alkane content. The slope of the curve is used to characterize mixtures of alkanes according to their EACN. Only a slight increase in the alcohol partitioning into the oil phase is observed with an increase in the EACN. The titration curve is also used to estimate pyrene partitioning in the interface and oil phase of a W/O microemulsion. Consequently, pyrene fluorescence can be used to estimate the partitioning of n-Hexanol in the interface and oil phase.

CHAPTER I

INTRODUCTION

1.1 Oil Recovery Processes

Crude oil is not a recoverable energy resource. On the average only 35% of the crude oil present in the petroleum reservoir is produced by the present oil production methods. These facts had not been seriously considered by the world until the last decade after the oil embargo exercised by the OPEC nations in 1973. Thenceforth, many enhanced oil recovery research programs were initiated in laboratories worldwide.

The production of crude oil from the petroleum reservoir can be divided into three stages: primary, secondary and tertiary. Primary production commonly refers to production of oil from a reservoir by natural mechanisms to replace the volume of oil produced. These mechanisms include pressure of the entrapped gases and water encroachment (Greenkorn, 1983). Secondary oil recovery is a term used to describe the displacement of oil by injection of water into the reservoir. Water injection increases the pressure required to drive the oil through the porous rocks and thus more oil is recovered. At the end of this stage about 67% of the oil still remains in the pores

(Geffen, 1973; Roy et al., 1977; Sharp, 1975). Tertiary oil recovery methods are applied after the reservoir no longer produces oil economically by water flooding. Some of the tertiary recovery processes are as follows (Johansen, 1979):

1) Chemical injection methods in which chemical slugs in water and/or oil are injected into the oil reservoir in order to force the oil through to the producing wells. This category includes the processes such as caustic, micellar, surfactant and polymer flooding.

2) Thermal recovery methods to inject or to generate heat in the reservoir in order to lower the viscosity of the oil. Steam flooding, cyclic steam injection and in situ combustion processes are in this class.

3) Miscible-fluid displacement, which includes the injection of carbon dioxide, liquid hydrocarbons or other gases into the reservoirs.

The suitability of a given tertiary oil recovery process depends on specific characteristics of the oil field. The chemical flooding is suitable for light oils (< 28° API), the thermal processes for heavy oils (> 28° API), and miscible-fluid displacement methods for limestone reservoirs of light oil.

1.2 Oil Recovery by Surfactant Flooding

A surfactant molecule has two functional parts, namely, a hydrophilic (water-soluble) or polar part and a lipophilic (oil-soluble) or non-polar part. The lipophilic segment is usually a long hydrocarbon chain, while the hydrophilic group can be anionic, cationic, nonionic or zwitterionic. Over a narrow concentration range, a water-soluble surfactant exhibits an abrupt change in solution properties such as surface tension, viscosity, electrical conductivity and density. This concentration is named the Critical Micelle Concentration (CMC). The observed sharp changes in the solution properties are due to the formation of aggregates, called micelles.

Micelles are formed as a result of two opposing forces, an attractive force favoring aggregation and a repulsive force that prevents the growth of the aggregates to large size (Tanford, 1980, p. 43). The attractive force arises from the "Hydrophobic Effect" which acts on the hydrocarbon chains of the surfactant (Kauzman, 1959; Nemethy, 1967; Tanford, 1980), while the repulsive force comes from the head groups of surfactant monomers.

Micelles are in general spherical and their size is about 40 to 100 Å in diameter. Surfactants in organic solvents form reverse micelles that are normally smaller in size than normal micelles. The orientation of surfactant molecules in reverse micelles is opposite to that of normal micelles. The polar groups are oriented outward towards water and hydrocarbon chains form the interior of the normal micelles, whereas the polar groups are in the interior and the hydrocarbon chains are toward the solvent phase in the reverse micelles.

Most of the enhanced oil recovery (EOR) formulations consist of anionic surfactants such as petroleum sulfonates, or in some cases mixed with nonionic surfactants. One of the most important and desirable characteristics of the surfactants used for oil recovery is that they produce ultralow interfacial tension (IFT) at the oil/brine interface ($\cong 10^{-3}$ dynes/cm) under reservoir conditions. Surfactant formulations employed in EOR are either at low (0.1% to 1%) or at high (5% to 30%) surfactant concentrations. At low concentrations, phase volume changes due to mass transfer during equilibration are not significant. Although surfactant formulations of low concentration are effective in lowering the interfacial tension between oil and water to ultralow values of less than 0.001 dyne/cm, they are not employed for EOR due to the lack of mobility and the adsorption and/or precipitation of surfactants resulting in higher interfacial tension (Chiang, 1979; Chiang and Shah, 1981; Gogarty, 1978; Goldberg, 1977; Hsieh and Shah, 1977; Morgan et al., 1979; Widmeyer et al., 1977). However, both high and low surfactant concentration systems are relevant to EOR since the chemical slug that starts at high surfactant concentration ends up in low concentration levels due to various surfactant loss mechanisms. At higher surfactant concentrations, phase volume changes are observable and important. The majority of surfactant floods carried out employed the high surfactant concentration system. The interfacial tension-lowering by such systems is accomplished by the formation of a third phase that contains almost all the surfactant along with large amounts of solubilized water and hydrocarbon. This third phase is called the middle-phase microemulsion.

1.3 Role of Interfacial Tension in EOR

The production of very low interfacial tension between the displacing aqueous phase and the reservoir crude oil is probably the primary recovery mechanism of surfactant water-flooding (Foster, 1973). Several researchers have indicated the achievement of ultralow tension by the use of anionic surfactants in both low and high surfactant concentration systems (Chan and Shah, 1980; Doe et al., 1977; Hsieh and Shah, 1977; Puig et al., 1979; Wade et al., 1978). The flow of oil inside the porous medium is a function of the velocity and viscosity of the displacing fluid (viscous force), while the displacement of oil ganglia is opposed by capillary forces. Capillary forces are proportional to the interfacial tension between the oil and displacing fluid. Thus, to mobilize the oil ganglia either viscous forces have to be increased or capillary forces have to be decreased. Practically, the velocity and viscosity of the displacing fluid could be changed only within narrow limits under reservoir conditions. Therefore, the feasibility of mobilizing the oil ganglia relies upon the reduction of interfacial tension.

Darcy-law pressure gradient (viscous) forces and interfacial-tension-controlled capillary forces are coupled in the most important dimensionless group that controls the process of oil mobilization, the capillary number N_c (Melrose and Brandner, 1974). The capillary number is the ratio of viscous forces to capillary forces (Abrams, 1975; Catchpole and Fulford, 1966; Foster, 1973; LeFebvre du Prey, 1966).

It is written as

$$N_c = \frac{v\mu}{\phi\gamma}$$

where

v is the flow velocity in cm/sec,

μ is viscosity of displacing fluid in centipoise,

ϕ is porosity of porous media, and

γ is the oil/water interfacial tension in dyne/cm.

For realistic values of the above mentioned parameters, N_c is in the order of 10^{-6}. A necessary value of N_c for oil mobilization is in the order of 10^{-3}. Thus, a reduction in the IFT by at least three orders of magnitude is essential (Melrose and Brandner, 1974; Taber, 1969).

Interfacial tension values below 10^{-1} dyne/cm significantly change the relative oil-water permeabilities

(Amaefule and Handy, 1982). It has been shown that a decrease in the IFT (increase in N_c) leads to an increase in relative oil/water permeabilities, a decrease in the residual oil saturations and an increase in the total relative mobilities.

To achieve ultralow interfacial tension, five necessary conditions have been proposed (Noronha, 1980; Shah, 1981).

1) The total surfactant concentration should be above the apparent CMC in the aqueous phase.

2) The surfactant should be soluble in both the oil and the aqueous phases.

3) Micelles in the aqueous phase ought to be able to solubilize oil.

4) The aqueous phase salinity should be near the first critical electrolyte concentration.

5) In the region of the ultralow IFT, the surfactant partition coefficient should exhibit a sharp increase.

It should be stressed that the very low interfacial tensions between the surfactant slug and the residual oil and between the surfactant slug and drive fluid (usually a polymer solution) have to be maintained throughout the recovery process (Reed and Healy, 1977; Taber, 1969). This requirement can be adversely affected by surfactant losses. If surfactant losses are excessive, the surfactant slug is depleted, and consequently interfacial tension becomes high, causing re-entrapment of residual oil in the reservoir (Glover et al., 1978). Thus, minimal surfactant loss to reservoir rock is an essential requirement for successful oil recovery (Ahearn, 1969; Gale and Sandvick, 1973; Pursley and Graham, 1975).

Recently, an empirical relationship between surfactant retention and final residual oil saturation has been described (Presley, 1983). Such relationship was used to predict the performance of that oil recovery process. Previous publications have described several mechanisms that are responsible for loss of surfactants in porous media (Bae and Petrick, 1977; Foster, 1973; Hill et al., 1973; Hurd, 1976; Johnson, 1957; Lawson, 1976; Malmberg and Smith, 1977; Somasundaran and Hanna, 1977; Trogus et al., 1977; Trushenski, 1977; Trushenski et al., 1974). These include precipitation, adsorption, partitioning into the oil phase and entrapment of immiscible microemulsion phases.

Adsorption of surfactants on solids is the result of interactions of the surfactant species or its complexes with the chemical ions on or near the solid surface (Somasundaran and Hanna, 1977). Many other factors affect surfactant adsorption on reservoir solids, among which are solution pH, temperature, ionic strength and surfactant equivalent weight and structure. Sacrificial agents like sodium bicarbonate could be used to minimize surfactant adsorption (Bae and Patrick, 1977). Surfactants precipitate due to high concentrations of monovalent and polyvalent cations. It has been found that the use of ethoxylated alcohols and phosphated esters can significantly reduce surfactant precipitation (Dauben and Froning, 1971; Sharma et al., 1983).

1.4 Phase Behavior of Surfactant Systems

Microemulsions are thermodynamically stable isotropic dispersions of two relatively immiscible liquids, consisting of microdomains of one or both liquids stabilized by an interfacial film of surface-active molecules (Johnson and Shah, 1984; Leung et al., 1985; Pithapurwala, 1984, p. 47).

Microemulsions relevant to oil recovery processes consist of five components: oil, water, salt, surfactant (usually a petroleum sulfonate) and a cosolvent (usually a short chain alcohol). Salt and water are frequently treated as a pseudocomponent, allowing the microemulsion to be represented by four components. Moreover, if specific ratios of surfactant to cosurfactant are taken, then the phase behavior of the system can be represented by a pseudoternary diagram.

The microemulsion (surfactant) slug, once injected into the porous medium for oil recovery, solubilizes oil, reduces the interfacial tension between the oil and water-rich phases, and displaces the oil and water as it progresses through the porous medium (Salter, 1978). During this process, the microemulsion and reservoir fluids mix and hence the composition of the microemulsion changes. This consequently leads to separation into two or more phases (Davis and Jones, 1968; Healy and Reed, 1977; Healy et al., 1975). Therefore, one has to know the phase behavior of surfactant systems in order to understand the displacement mechanism, to model process efficiency and to screen suitable microemulsion systems for an optimal design of the oil recovery process.

The phase behavior of surfactant, oil and brine systems may take any of the three forms represented in the ternary diagrams shown in Figure 1.1 according to their salinity (Winsor, 1948, 1950, 1968). Figure 1.1a is a schematic representation of the phase behavior at low salinities. At high surfactant concentrations, the system is a single phase, below which two phases coexist in equilibrium. The lower phase consists of almost all of the surfactant and solubilized oil in brine, whereas the upper phase is predominantly oil.

At high salinities, the system below the single-phase region also exhibits two phases. The lower phase is predominantly brine, whereas the upper phase consists of oil, most of the surfactant and solubilized brine.

At moderate salinities, three phases appear. A middle-phase microemulsion, consisting of nearly all the surfactant with solubilized oil and brine, remains in equilibrium with the excess brine and oil phases. The microemulsions formed in the low-salinity region are called Winsor's Type I, lower-phase or underoptimum microemulsions. Those in the moderate-salinity region are called Winsor's Type III,

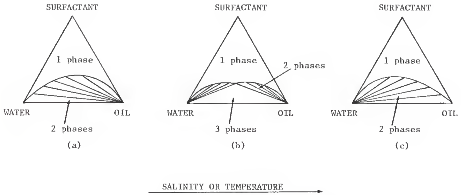

Figure 1.1. Illustration of Phase Behavior Using Pseudoternary Diagrams to Represent Winsor's Type I (a), III (b), and II (c) Systems.

middle-phase or optimum microemulsions, whereas those in the high salinity region are called Winsor's Type II, upper-phase or overoptimum microemulsions (Hirasaki et al., 1983; Reed and Healy, 1977).

The three-phase system containing the middle-phase microemulsion is very important in relation to tertiary oil recovery. The salinity at which the middle phase solubilizes equal volumes of oil and brine is called the phase behavior-optimal salinity. At the optimal salinity, the interfacial tension of the middle-phase microemulsion with excess oil is the same as that with excess brine (Reed and Healy, 1977). The volume of solubilized oil or brine per unit volume or weight of surfactant is referred to as the solubilization parameter. Surfactant systems with higher solubilization parameter are promising for the oil recovery process because they exhibit lower interfacial tension values (Saito and Shinoda, 1970). Also, it has been found experimentally and theoretically that the greater the solubilization parameter, the lower is the interfacial tension (Barakat et al., 1983; Graciaa et al., 1982; Huh, 1979).

On both theoretical (Miller and Neogi, 1980, Miller et al., 1977) and experimental (Benton et al., 1982) grounds, the middle-phase microemulsion was found oil continuous near the upper-phase boundary, and water continuous near the lower-phase boundary. However, away from these vicinities, several possible structures have been proposed for the middle-phase microemulsion. Among these are 1) A bicontinuous structure of oil and water with intervening surfactant layers (Scriven, 1977); 2) A mixture of water-external and oil-external microemulsions (Miller and Neogi, 1978; Winsor, 1954, p. 68); 3) A water-external microemulsion containing dispersed oil droplets (Hsieh, 1977); 4) A lamellar structure of alternating layers of oil and brine (Friberg et al., 1976; Shinoda and Friberg, 1975).

In most surfactant formulations for enhanced oil recovery, a cosurfactant is added in addition to the surfactant. A cosurfactant is often a short chain alcohol such as isopropanol, n-butanol, isobutanol or an isomer of pentanol or hexanol. The addition of alcohol promotes the lowering of interfacial viscosity and interfacial tension between oil and the surfactant formulation and the formation of high viscosity birefringent structures or gels (Reed and Healy, 1977; Ruckenstein and Krishnan, 1980; Wasan et al., 1978). Besides these effects, the addition of alcohol also decreases and retards the precipitation of surfactant due to the high concentration of multivalent cations. It has been mentioned that alcohol stabilizes the microemulsions (Baviere et al., 1981). However, the mechanism by which alcohol acts to stabilize microemulsions is not fully understood (Baviere et al., 1981).

1.5 Role of Coalescence Phenomena in Enhanced Oil Recovery

The most important property of a surfactant flooding process is its capability to initiate and propagate an oil bank (Wasan et al., 1978, 1979). As the surfactant formulation is injected into the porous medium, it contacts the entrapped oil as well as connate brine. If a stable emulsion results, then poor oil recovery efficiency is expected (Strange and Talash, 1977; Whitley and Ware, 1977; Widmeyer et al., 1977). On the other hand, if spontaneous emulsification followed by a rapid coalescence is observed in the system, then a better oil recovery is attained (Childress, 1975; Schechter and Wade, 1976).

It has been suggested that the coalescence of displaced oil ganglia can lead to oil bank formation (Wasan et al., 1979). Many factors could influence the coalescence of droplets, among which are the interfacial tension, interfacial charge and interfacial viscosity. The rate of coalescence is measured by determining the time required for the droplets to coalesce (Aderangi, 1978; Wasan et al., 1978). It is also measured by the time required for complete or partial separation of the phases involved (Baldauf et al., 1982; Vijayan et al., 1981; Vinatieri, 1980).

The phase behavior of a surfactant system is related to its coalescence. It has been reported that the middle-phase microemulsion shows the fastest rate of coalescence (Vinatieri, 1980). The lower-phase microemulsion exhibits extremely long times for coalescence.

1.6 The Equivalent Alkane Carbon Number Concept

Two characteristics of crude oil hinder its use as the model oil in tertiary oil recovery laboratory experiments. Crude oil is dark in color which makes observation of phase-volume changes difficult. In addition to its dark color, crude oil is sometimes so viscous that equilibrium during interfacial tension measurements is attained very slowly (Morgan et al., 1979). Therefore, the crude oil is generally simulated by synthetic oil mixtures, e.g., a pure hydrocarbon such as decane or dodecane or a mixture of hydrocarbons (Healy and Reed, 1977).

The equivalent alkane carbon number (EACN) concept has been established from the interfacial tension measurements of a large number of binary mixtures of various hydrocarbons and some of their isomers (Cash et al., 1977; Cayias et al., 1976a,b). Interfacial tension was measured for fresh oil contacting the surfactant solution. The EACN of a mixed oil system is written as

$$(\mathrm{EACN}) = \sum_{i}^{N} (\mathrm{EACN})_i \, X_i$$

where EACN_i is the equivalent alkane carbon number of component i, X_i is the mole fraction of component i, and N is the number of components in the mixture. According to the EACN concept, a pure alkane can simulate crude oil in laboratory experiments.

The EACN concept was applied to phase behavior where the mixing rule for a hydrocarbon mixture involved calculation of a mole fraction weighted-average equivalent carbon number (Salager et al., 1979). Also, the slope of the lower-phase boundary, a property of the phase diagram, was found to be a linear function of the alkane carbon number (ACN) for pure hydrocarbons and the EACN for mixtures of pure hydrocarbons (Shah et al., 1981).

However, such parameters as alcohol type, crude oil composition and water to oil ratio could have an effect on the EACN of a crude oil (Tham and Lorenz, 1981a). Moreover, the equilibration time can have an effect on both interfacial tension and the surfactant partitioning in the various phases of an oil/brine/surfactant/ cosurfactant system (Noronha, 1980).

The distribution of a surfactant in the aqueous and oil phases is measured by the partition coefficient (P.C.), which is the ratio of the surfactant concentration in the oil phase divided by that in the aqueous phase. The partition coefficient was correlated to the IFT (Baviere, 1976). The minimum in the IFT occurred when the P.C. was near unity. This was correlated to the maximum monomer concentration in the aqueous phase or the apparent CMC , and to the variation of the chemical potential of the surfactant (Shah et al., 1979; Wade et al., 1978, 1979). The minimum in the IFT, nonetheless, was reported to be reached as the partition coefficient starts to increase, i.e., as the surfactant begins to leave the aqueous phase (Noronha, 1980).

1.7 Scope

The objective of this study is to provide an understanding of the behavior of pure and mixed alkanes in relation to interfacial tension between oil and water, phase behavior, phase separation time, optimal salinity and oil displacement efficiency. The research conducted in this dissertation attempts to answer several important questions pertaining to surfactant formulations employed in tertiary oil recovery and the use of mixed hydrocarbons to simulate the oil component. Some of these questions are as follows:

1) In equilibrated systems, does a hydrocarbon mixture attain the same interfacial tension as its equivalent pure hydrocarbon at any salinity?

2) Are there differences in the optimal salinity, the salinity range of three-phase region and the coalescence behavior of a surfactant system when pure or mixed alkanes are used?

3) Does a surfactant formulation solubilize a hydrocarbon mixture as one component?

4) Is the oil displacement efficiency obtained by the use of a surfactant formulation of a pure alkane identical to that of an equivalent alkane mixture?

5) What is the effect of the cosurfactant structure on the phase behavior and oil displacement efficiency of a surfactant slug?

6) Can pyrene fluorescence be used to determine alcohol partitioning in the oil phase and interface of a microemulsion?

7) Is the concept of the equivalent alkane carbon number (EACN) valid in modeling crude oil or a mixture of alkanes?

Chapter II describes studies on a low surfactant concentration system. The effect of salinity on interfacial tension and surfactant partitioning for both pure and mixed alkanes systems is investigated.

In Chapter III, the phase behavior of high surfactant concentration systems is reported. The oil employed in this study is pure or mixed alkanes of the same equivalent alkane carbon number. The effect of the EACN on optimal salinity, the salinity range of the three-phase region and the separation time of the various phases involved is investigated.

Chapter IV deals with the effect of salinity and the cosurfactant structure on oil displacement efficiency. The validity of the EACN concept for an oil displacement experiment is tested. Selection criteria for a surfactant slug for optimal oil recovery are proposed.

Chapter V focuses on single-phase microemulsions. The molar ratio of alcohol per surfactant to oil per surfactant is used to characterize pure and mixed alkanes of the same equivalent alkane carbon number. A pyrene fluorescent probe is employed to measure the alcohol-to-oil ratio in the oil phase of a microemulsion.

Finally, Chapter VI summarizes the conclusions from the entire study and provides recommendations for future research in this area.

CHAPTER II

INTERFACIAL TENSION AND PARTITION COEFFICIENT OF SURFACTANT IN SINGLE AND MIXED ALKANE-CONTAINING SYSTEMS

2.1 Introduction

The importance of low surfactant concentration systems of surfactant concentrations < 1% (wt) is evident from its ability to lower the interfacial tension between oil and water to ultralow values of less than 0.001 dyne/cm. The attainment of ultralow interfacial tension is important for enhanced oil recovery by surfactant flooding. Indeed, high efficiency of tertiary oil recovery was obtained upon employing low surfactant concentrations (0.05 wt % TRS 10-80 and 0.1 wt % TRS 10-410) when mass transfer limitation was eliminated (Chiang and Shah, 1981).

The major goal to the research presented in this chapter is to delineate the effect of the equilibration procedure and the NaCl concentration on the magnitude of the interfacial tension isotherm and on the surfactant partitioning into the aqueous phase and the oil phase. The oil phase is represented by pure (single) or mixed alkanes.

The role of equilibration procedure on interfacial tension and surfactant partitioning has been extensively studied by Chan and Shah (1980), and by Noronha (1980). Chan and Shah (1980) determined the separate contributions of the surfactant (TRS 10-80) dissolved in the oil and the brine phases (1% NaCl) to the interfacial tension. The interfacial tension was measured for equilibrated n-octane contacted with a 1% NaCl solution and for an equilibrated aqueous phase against fresh n-octane as well as for both equilibrated n-octane and aqueous phases. The results suggest that the aqueous phase is predominantly responsible for the ultra-low interfacial tension attainment. Figure 2.1 is a representation of these results. An important conclusion from this figure is that the equilibration can affect the interfacial tension depending on the surfactant concentration used. Noronha (1980) investigated separately the various processes that make up the equilibration procedure. It was observed that the extent of mixing is the controlling factor and that the equilibration procedure has a greater effect on the partition coefficient and only a minor effect on the interfacial tension.

It is well known that the presence of electrolytes reduces the critical micelle concentration (CMC) of ionic surfactants, reduces the thickness of the electrical double layer around micelles, increases the micellar aggregation number, lowers the surface and interfacial tension of surfactant solutions and induces a shift in surface tension and interfacial tension isotherms toward lower surfactant concentrations.

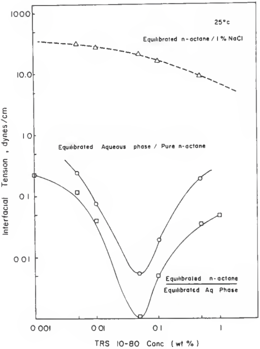

Figure 2.1. Interfacial Tension for TRS 10-80 in 1% NaCl Solution with n-Octane. (Chan and Shah, 1980) Reproduced by permission.

The equivalent alkane carbon number concept was first introduced by Cayias et al. (1976a,b), who observed that for a given electrolyte concentration, aqueous petroleum sulfonate surfactants in contact with alkanes, alkylbenzenes, or alkylcyclohexanes as the oil phase yield low interfacial tension for only a single member of each homologous hydrocarbon series. For a particular equivalent weight surfactant and electrolyte concentration, the three hydrocarbons might typically be octane, octylbenzene, and butylcyclohexane. It was further shown that appropriate mixtures of other hydrocarbon members will produce low interfacial tension if the average molecular weight is identical to octane and if phenyl and cyclohexyl groups are assumed to contribute zero and four carbons, respectively, to the attached alkyl side chains. Note that their interfacial tension measurements were obtained by contacting the surfactant solution with fresh hydrocarbons where it was assumed that equilibrium was reached during the measurements.

2.2 Experimental

A commercial petroleum sulfonate, TRS 10-80 (average molecular weight = 420), obtained from Witco Chemical Company, was used as received. The manufacturer specifications for this surfactant are given in Table 2.1. The oils used were a homologous series of alkanes with chain lengths from C_6 to C_{16} and their mixtures. All the oils

Table 2.1. Compositional Assay of TRS 10-80 Petroleum Sulfonate (supplied by Witco Chemical Co.)

	%
Percent Active Sulfonate	80
Free Oil	7-8
Water	10-12
Inorganic Salt	1.0

were > 99% pure and were obtained from Fisher Scientific Company. The concentration and labeling of alkane binary mixtures are shown in Table 2.2.

The systems were prepared by dissolving the surfactant (0.4%) in distilled water, diluting it to 0.2 wt % by NaCl solution to the desired salt concentration and then adding an equal volume of oil in 20 ml tubes and thus the water to oil ratio (WOR) was equal to 1.0. The tubes were then shaken in a multipurpose rotator (10 rpm) for 24 hours and then left for two weeks or more to thoroughly equilibrate. All measurements were performed on samples of the clear aqueous and oil phases separated at the bottom and top of the tubes, respectively. The surfactant and NaCl concentrations specified refer to their initial concentration in the aqueous phase. The tubes needed several weeks or months for equilibration. Many samples ended up with a thick white

Table 2.2. Mixed Hydrocarbon Labeling and Preparation.

Oil #	Symbols used in Figures 2.9-2.14	EACN	Mixture of	Mole Fraction of First Component
8		8	C_8	1.00
8A		8	C_6 and C_{14}	0.75
8B		8	C_6 and C_{16}	0.80
8C		8	C_6 and C_{10}	0.50
8D		8	C_7 and C_9	0.50
8E		8	C_7 and C_{11}	0.75
10		10	C_{10}	1.00
10A		10	C_6 and C_{14}	0.50
10B		10	C_6 and C_{16}	0.60
10C		10	C_8 and C_{12}	0.50
10D		10	C_9 and C_{11}	0.50
10E		10	C_8 and C_{16}	0.75
12		12	C_{12}	1.00
12A		12	C_6 and C_{14}	0.25
12B		12	C_6 and C_{16}	0.40
12C		12	C_{10} and C_{14}	0.50
12D		12	C_9 and C_{15}	0.50
12E		12	C_8 and C_{16}	0.50
14		14	C_{14}	1.00
14A		14	C_7 and C_{16}	0.222
14B		14	C_9 and C_{15}	0.167
14C		14	C_{13} and C_{15}	0.50
16		16	C_{16}	1.00

interface with a turbid color on either side of it--that is, in both the aqueous and the oil phases. The reproducibility of the systems seems to be highly unreliable.

2.2.1 Interfacial Tension Measurements

Interfacial tension between two liquid phases was measured by a spinning drop interfacial tensiometer developed by Cayias et al. (1975). The procedure followed was to fill a capillary tube with the more dense liquid and then inject a drop of the less dense liquid. The tube was then rotated horizontally causing the drop to elongate to an elliptical shape. The methodology of this interfacial tension measuring technique is based on measuring both the length and width of the drop.

When the length of the drop is greater than the width by 4 times or more, the interfacial tension can be accurately represented by the following equation:

$$\gamma = 0.01322\ \Delta\rho\omega^2 d^3$$

where

γ is the interfacial tension in dynes/cm,

$\Delta\rho$ is the difference in densities of the two liquids in gm/cm^3,

d is the measured diameter of drop in cm, and

ω is the is the angular velocity of rotation in sec^{-1}.

The interfacial tension measurements were carried out at room temperature (24 ± 1°C). The width of the drop was recorded several times during the measurements and the used value in the calculations was the one which remained constant with time. The interfacial tension values are reproducible within 5%.

2.2.2 Analysis of Surfactant

The concentration of a petroleum sulfonate (an anionic surfactant) was determined by a two phase titration with cationic surfactant as titrant. The end point was detected by the mixed indicator dimidium bromide (cationic) disulphine blue VN 150 (anionic). This titration method is also called the Herring method (Herring, 1962).

The cationic titrant used was a benzyl derivative, Hyamine 1622, while the two phases were an aqueous phase and a chloroform phase. The acid indicator solution was prepared by adding 20 ml of the indicator to 200 ml of distilled water in a 500 ml flask. Then 20 ml of 2.5 M sulphuric acid solution was added and the solution was diluted to volume with distilled water. The molarity of Hyamine 1622 was standardized by a sodium dodecyl sulphate solution as described elsewhere (Longman, 1975, p. 236).

The surfactant concentration was determined by adding 10 ml of distilled water to the surfactant solution (usually 5 ml), 10 ml of the acid indicator and 15 ml of chloroform. At this stage the chloroform phase was pink in color.

Titration was carried out then with the standardized Hyamine 1622 solution until the chloroform phase color turned to light blue. The surfactant concentration was calculated using the following equation:

$$\text{Anionic surfactant (\% by weight)} = \frac{M_1 V_2 C_2}{10\ V_1}$$

where M_1 is the molecular weight of anionic surfactant,

V_2 is the volume of Hyamine 1622, ml,

C_2 is the molarity of Hyamine 1622, and

V_1 is the volume of sample, ml.

The volumes of the two phases were kept constant throughout the entire surfactant concentration measurement in order to secure the same accuracy. Up to a surfactant concentration of 0.001% in a 5 ml sample could be detected by this method.

Chloroform of A.R. grade was obtained from Mallinckrodt, Inc. Hyamine 1622, sodium dodecyl sulphate and the mixed indicators were obtained from BDH Chemicals Ltd.

2.3 Effect of NaCl Concentration on Pure Alkane Systems

At low NaCl concentrations in oil/brine/surfactant systems, the interfacial tension between the aqueous phase and the oil phase is quite high. As the salinity increases, the interfacial tension reaches a minimum value, then increases as the salinity is further increased. As shown in Figures 2.2 through 2.4, this minimum occurs at a specific salinity for each pure alkane. This salinity of minimum interfacial tension, which is called optimal salinity hereafter, increases slightly as the oil chain length increases from octane to hexadecane.

Furthermore, it is observed that the interfacial tension value is in the millidyne/cm range only for octane which agrees with the earlier findings (Cash et al., 1976, 1977). This behavior is attributed to the equivalent weight of the surfactant used (eq. wt = 420) (Klaus et al., 1983). If a higher equivalent weight petroleum sulfonate surfactant is employed, then the ultralow interfacial tension minimum will occur at a higher oil chain length than that of octane (Wade et al., 1976). The partitioning of the surfactant in the aqueous and oil phases and the partition coefficient are shown in Figures 2.5 through 2.8 for octane, decane, dodecane and tetradecane, respectively, where the partition coefficient is a dimensionless quantity, defined as the surfactant concentration in the oil phase divided by that in the aqueous phase.

$$\text{P.C.} = \frac{\text{Surfactant concentration in the oil phase}}{\text{Surfactant concentration in the aqueous phase}}$$

$$= \frac{C_{oil}}{C_{aq}} \ .$$

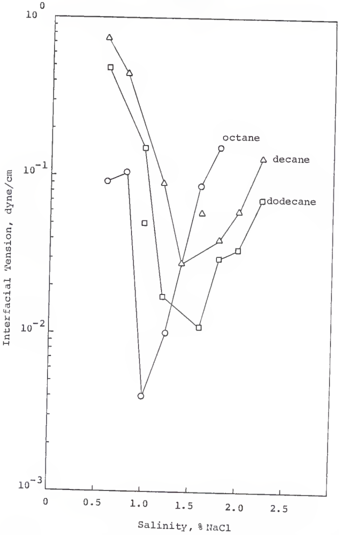

Figure 2.2. Effect of Salinity on the Interfacial Tension for the System 0.2% TRS 10-80/Brine/Alkane (WOR = 1).

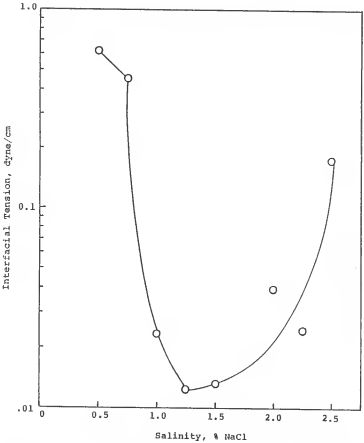

Figure 2.3. Effect of Salinity on Interfacial Tension for the System 0.2% TRS 10-80/Brine/Tetradecane (WOR = 1).

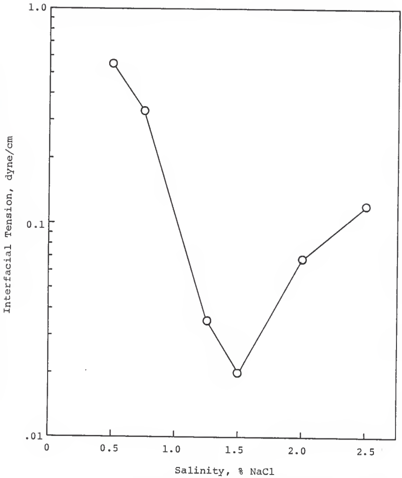

Figure 2.4. Effect of Salinity on Interfacial Tension for the System 0.2% TRS 10-80/Brine/Hexadecane (WOR = 1).

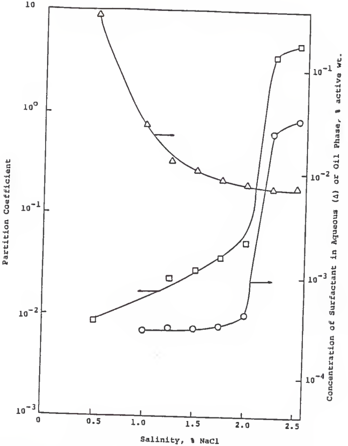

Figure 2.5. Effect of Salinity on the Partitioning of TRS 10-80 in the System 0.2% TRS 10-80/ Brine/Octane.

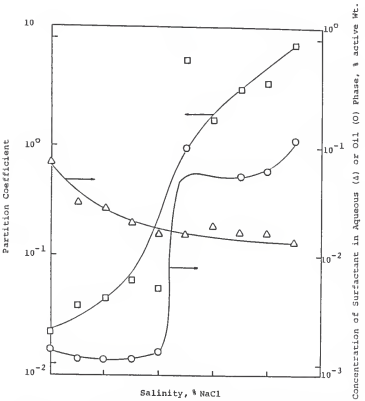

Figure 2.6. Effect of NaCl Concentration on the Partitioning of TRS 10-80 in the System 0.2% TRS 10-80/Brine/Decane (WOR = 1).

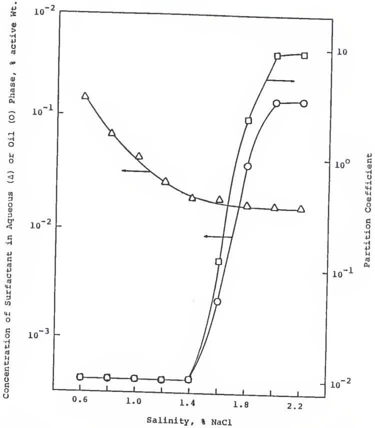

Figure 2.7. Effect of Salinity on TRS 10-80 Partitioning in the System 0.2%TRS 10-80/Brine/Dodecane (WOR = 1).

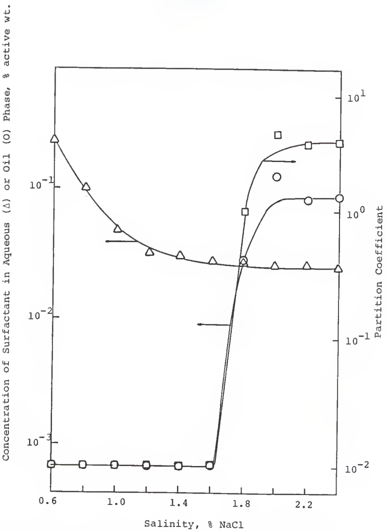

Figure 2.8. Effect of Salinity on the Partitioning of TRS 10-80 in the System 0.2% TRS 10-80/ Brine/Tetradecane (WOR = 1).

The increase in salt concentration results in two effects; micellization and salting-out (Beunen and Ruckenstein, 1982; Ruckenstein and Krishnan, 1980). As the concentration of salt is increased, the critical micelle concentration decreases due to the shielding of the coulombic repulsion between the head groups of the surfactant. Accordingly, more surfactant molecules can aggregate as micelles and, therefore, less free molecules of the surfactant are available for adsorption at the interface and the interfacial tension should increase. But simultaneously, another effect is caused by the increase in salinity, i.e., the salting-out process. Salting-out causes a decrease in the maximum solubility of surfactant in water, and hence surfactant molecules are driven to the interface upon an increase in the salt concentration (Bockris and Reddy, 1977).

The second effect outweighs the first one as seen by the interfacial tension. Upon further increase in the electrolyte concentration, the surfactant molecules are driven from the interface to the oil phase and hence the interfacial tension increases. Thus, it is mostly the salting-out of surfactant from brine and salting-in into oil which lead to the minimum in interfacial tension curve when salinity is increased.

As can be seen from the figures of the surfactant partitioning, at low salinity, most of the surfactant remains in the aqueous phase. As the NaCl concentration is increased, a pronounced decline in the surfactant concentration in the aqueous phase takes place. On the other hand, the surfactant concentration in the oil phase remains very low and only starts to rise beyond the salinity of minimum interfacial tension. This behavior implies that the salting-out process is dominating at salinities around the optimal salinity. The decrease in surfactant concentration in the aqueous phase correlates with the increased adsorption at the interface leading to lower interfacial tension values.

Beyond the optimal salinity, the surfactant concentration in the oil phase continues to increase, while that in the aqueous phase remains constant. Therefore, fewer surfactant molecules are adsorbed at the interface, and consequently the interfacial tension rises.

The partition coefficient curves exhibit a sharp increase near optimal salinity. They are primarily influenced by the partitioning of surfactant in the oil phase.

2.4 Effect of NaCl Concentration on the Mixed Alkane Systems

In this section, studies parallel to those in the previous section were investigated with the following change. Binary mixtures of alkanes were selected to represent octane, decane or dodecane according to their oil chain length so that

$$(\text{Oil chain length})_{\text{mixture}} = \sum_{i}^{N} X_i \ (\text{Oil chain length})_i$$

where X_i is the mole fraction of component i, and N is the total number of components of alkanes. The interfacial tension measurements for these oil mixtures equilibrated with surfactant solutions at salinities of 0.6%, 1.0%, 1.2%, 1.4%, 1.6% and 1.8% NaCl are shown in Figures 2.9 through 2.14, respectively.

These figures clearly show that binary mixtures of hydrocarbons of equivalent alkane carbon number do, indeed, attain the same interfacial tension at all salinities studied (to within one order of magnitude).

It is worth mentioning that even though tubes were left for months, some of the system may have not reached true equilibrium. The aqueous and oil phases looked turbid. Other systems have developed a thick, white interface of about 2 ml thickness (0.4 ml volume). These problems caused enormous variations in surfactant partitioning in the aqueous and oil phases when the mixed alkanes were used. It was very difficult to take a clear sample of either the aqueous phase or the oil phase for surfactant concentration measurements. On the other hand, the interfacial tension measurements seem to be satisfactory due to the equilibration process that takes place during the interfacial tension measurements.

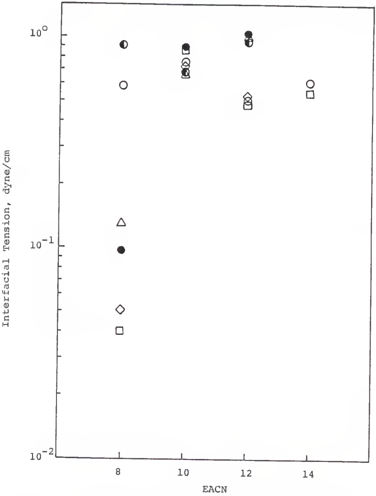

Figure 2.9. Effect of EACN on IFT for the System 0.2% TRS 10-80/0.6% NaCl/Oil (WOR = 1). See Table 2.2.

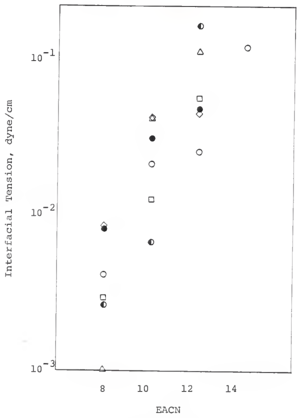

Figure 2.10. Effect of EACN on IFT for the System 0.2/TRS 10-80/1% NaCl Brine/Oil (WOR = 1). See Table 2.2.

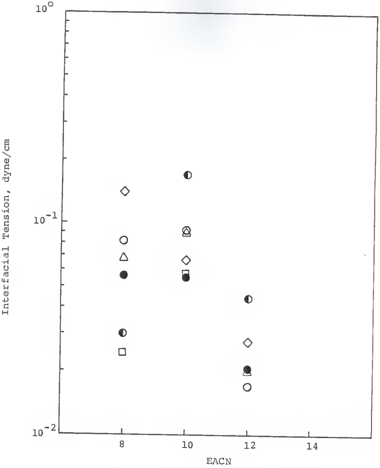

Figure 2.11. Effect of EACN on IFT for the System 0.2% TRS 10-80/1.2% NaCl Brine/Oil (WOR = 1). See Table 2.2.

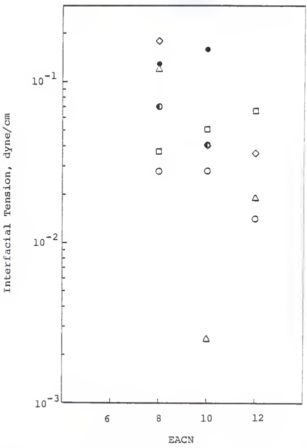

Figure 2.12. Interfacial Tension Variations with Binary Mixtures of Alkanes Used as Oil Phase in the System 0.2% TRS 10-80/1.4% NaCl Brine/ Oil (WOR = 1). See Table 2.2.

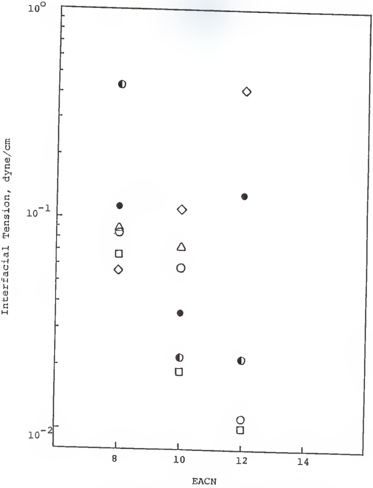

Figure 2.13. Effect of EACN on IFT for the System 0.2% TRS 10-80/1.6% NaCl Brine/Oil (WOR = 1). See Table 2.2.

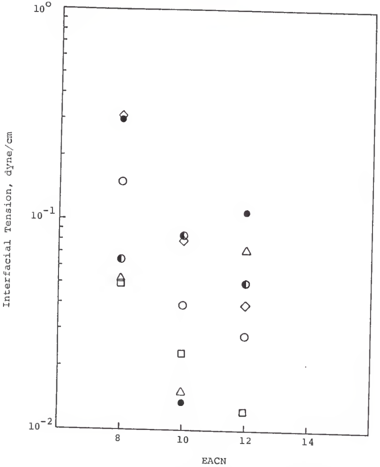

Figure 2.14. Effect of EACN on IFT for the System 0.2% TRS 10-80/1.8% NaCl Brine/Oil (WOR = 1). See Table 2.2.

2.5 Summary

The following are conclusions drawn from the results obtained in this chapter.

1. Interfacial tension of a system 0.2% TRS 10-80/brine/oil goes through a sharp minimum at a specific NaCl concentration. This is true for all alkanes used from octane to hexadecane.
2. Only the system with the EACN = 8 has a minimum interfacial tension in the range of 10^{-3} dyne/cm.
3. Interfacial tension minimum is caused presumably by the salting-out effect on surfactants.
4. The surfactant partitioning in the aqueous phase decreases gradually as the NaCl concentration increases.
5. Surfactant starts to migrate to the oil phase just above the optimal salinity.
6. Interfacial tension measurements confirm that binary mixtures of alkanes behave identically to their equivalent pure ones within the reproducibility limit of the experiments.

CHAPTER III

THE EFFECT OF SINGLE AND MIXED ALKANES ON PHASE BEHAVIOR AND PHASE SEPARATION TIME OF HIGH SURFACTANT CONCENTRATION SYSTEMS

3.1 Introduction

Successful tertiary oil recovery flooding relies highly on the ability of the employed surfactant/polymer system to initiate and propagate an oil bank which forms just ahead of the displacing fluid. The phase behavior, interfacial effects and rheological properties of the surfactant formulation and other phases present are among the primary determinants of oil bank formation and ultimately a better oil recovery efficiency process.

The phase behavior of a surfactant-containing system used in microemulsion flooding is near the Winsor's III region, where the three phases coexist in equilibrium (Winsor, 1948, 1950). Variables such as salinity, temperature, oil chain length, pressure, structure and concentration of surfactant and alcohol influence the phase behavior of a surfactant-oil-brine-alcohol system. At low salinities, equilibrating the system results in two phases; a lower surfactant-rich phase that is called lower-phase microemulsion due to the solubilization of oil by the surfactant-rich aqueous phase, and an upper phase consisting mostly of excess oil. As the NaCl concentration is increased, the system starts to exhibit three phases: a lower aqueous phase that is mostly brine, a surfactant-rich phase so-called middle-phase microemulsion and an upper phase, mostly excess oil. The system at high salinities becomes two phases, a lower-aqueous phase and an upper surfactant-rich phase that is called upper-phase microemulsion. The transition from lower-phase to middle-phase to upper-phase (l- to m- to u-) microemulsion can be characterized by changes in the interfacial tension and the solubilization parameter that is defined as the volume of solubilized oil or brine per unit volume of surfactant (Reed and Healy, 1977). Figure 3.1 illustrates the progression of phase volumes and interfacial tensions as a function of salinity. The vast importance of ultralow interfacial tension as a major factor toward successful tertiary oil recovery by surfactant flooding has been singled out by all the researchers in this field (Larson et al., 1982; Morgan et al., 1979; Reed and Healy, 1977; Shah, 1981).

The middle-phase microemulsion may exhibit ultralow interfacial tension towards both the upper-oil phase and the lower-aqueous phase. Moreover, it produces minimum interfacial tension when the system contains equal amounts of oil and brine at a specific salinity, as shown in Figure 3.1.

In this chapter, the effect of pure (single) and mixed hydrocarbons of various oil chain length on the phase

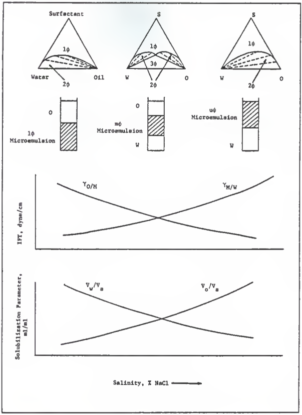

Figure 3.1. Schematic Diagram of a Typical Microemulsion Salinity Scan Showing the Progression of Phase Diagrams, Phase Volumes and Interfacial Tensions.

behavior will be investigated. These studies will include the range of the three-phase region salinity, optimal salinity and solubilization parameter. The rate of separation for the phases that appear as the salinity of the system is varied will also be studied. Whether a surfactant formulation can preferentially solubilize a component of the hydrocarbon mixture will be tested. The results may support the hypothesis that a mixture of pure hydrocarbons can be considered as a single component, oil (Salter, 1978).

These studies for the high surfactant concentration system are the most relevant to the design of an effective and successful surfactant slug.

3.2 Experimental

Two surfactant systems were used in this study, TRS 10-410 (Witco Chemical Company), a commercial surfactant (average molecular weight = 418), commonly used in tertiary oil recovery, and sodium stearate (ICN Pharmaceuticals, Inc., Plainview, N.Y.), a pure surfactant. Both surfactants were used as received. The manufacturer specifications for TRS 10-410 are listed in Table 3.1.

Alkanes used were of > 99% purity and were obtained from Fisher Scientific Company. Table 2.2 shows the mole fraction of the mixed alkanes and the labeling system adopted.

For the phase volume behavior studies, the surfactant and cosurfactant blends were mixed with equal volumes of

Table 3.1. Compositional Assay of the Petroleum Sulfontate (TRS 10-410) (Supplied by Witco Chemical Company).

	%
Active Sulfontate	62
Free Oil	33
Water	4-5
Inorganic Salt	0.1

Table 3.2. Optimal Salinity, Solubilization Parameter at Optimal Salinity and Salinity Range of Three-Phase Region Where Pure and Mixed Hydrocarbons Represents Oil Component.

System: TRS10-410(5wt.%)+Isobutanol(3%)+Brine+Oil(O/W=1/1 by vol.)

Oil#	Optimal Salinity	V_o/V_s or V_w/V_s at Opt. Sal.	Salinity Range of Three-Phase Region (% NaCl ± 0.05)
10	0.89	8.0	0.75 - 1.05
10A	0.87	8.1	0.75 - 1.05
10B	0.84	8.2	0.75 - 1.05
10C	1.02	6.7	0.85 - 1.25
10D	1.01	6.4	0.75 - 1.25
12	1.19	5.9	1.0 - 1.5
12C	1.25	5.3	1.1 - 1.7
12D	1.21	5.7	1.0 - 1.6
12E	1.19	5.5	1.1 - 1.6
14	1.48	4.4	1.2 - 2.1
14A	1.56	4.0	1.2 - 2.2
14C	1.50	4.2	1.2 - 2.2
16	1.85	3.0	1.4 - 2.7

brine of desired salinity and oil. For the TRS 10-410/isobutanol blend, a 15/9 (wt %) in doubly distilled water stock solution was prepared. Then samples from stock solution were diluted with brine of the desired NaCl concentration to make the final solution of 5/3 wt % of surfactant and cosurfactant. For the sodium stearate studies, 0.53 gram surfactant was added to 2.65 ml isobutanol, 7.5 ml oil and 7.5 ml of brine. All systems were prepared in individually calibrated tubes of 1 cm inside diameter and shaken for 24 hours in a multi-purpose rotator. Measurements of the phase separation were carried out by timing the separation of the oil and brine phases at various time intervals. Note that for the lower-phase microemulsion region the timing was carried out for oil separation and for the upper-phase microemulsion region it was carried out for the brine separation because each of these two regions consists of only two phases, a surfactant-rich phase and a second phase that is oil or brine.

All studies were performed at room temperature (24°±1.0°C). The molar ratio of the two alkane components in the mixed oil systems was determined by using a Perkin Elmer 900 chromatograph with a Supelco SP-2100 column and the flame ionization detector. The area produced for each peak was accurately calculated by the use of a Hewlett-Packard hp 3373B integrator. Concentrations were measured twice and the average value was taken.

3.3 Salinity Range of Three-Phase Region

As has been mentioned in Chapter I, most of the enhanced oil recovery methods involving surfactants produce in situ middle-phase microemulsions for oil displacement in porous media. The middle-phase microemulsion is formed only in a certain salinity range.

If the salinity range of the three-phase region is narrow, a perturbation in any physicochemical variable can shift a three-phase system to a two-phase system with high interfacial tension. This may adversely influence the oil displacement efficiency. Thus, it is important to study the effect of oil chain length on the salinity range of the three-phase region.

Figure 3.2 relates solubilization parameter, V_o/V_s or V_w/V_s (V_o = volume of solubilized oil, V_s = volume of surfactant in microemulsion phase and V_w = volume of solubilized brine in microemulsion phase), to salinity when decane and binary mixtures of alkanes averaging 10 in oil chain length were used. Details of how mixtures were prepared are available in Table 2.2.

Phase-volume changes with salinity for EACN = 12, 14 and 16 are respectively shown in Figures 3.3-3.4, 3.5-3.7, and 3.8. These figures reveal that the volume of solubilized oil continuously increases with an increase in the NaCl concentration. On the other hand, as salinity increases, the volume of solubilized brine continually decreases.

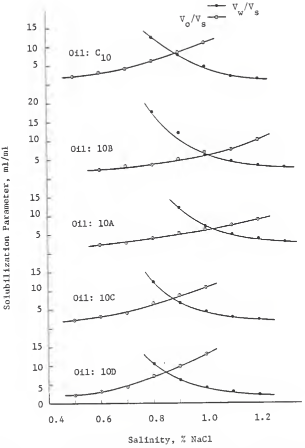

Figure 3.2. Effect of Salinity on Solubilization Parameter for the System 5% TRS 10-410 + 3% IBA + Brine + Oil. WOR = 1 and oil is represented by mixtures of alkanes having EACN = 10 (see Table 2.2).

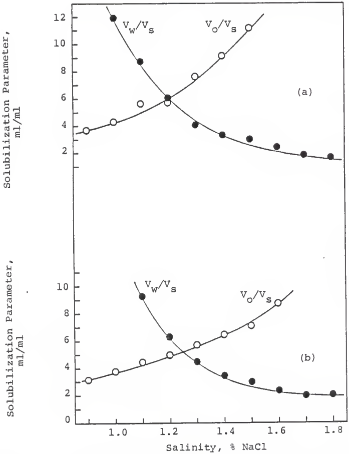

Figure 3.3. Effect of Salinity on Solubilization Parameter for the System 5% TRS 10-410 + 3% IBA + Brine + Oil. WOR = 1 and oil is (a) dodecane or (b) a mixture of decane + tetradecane of EACN = 12.

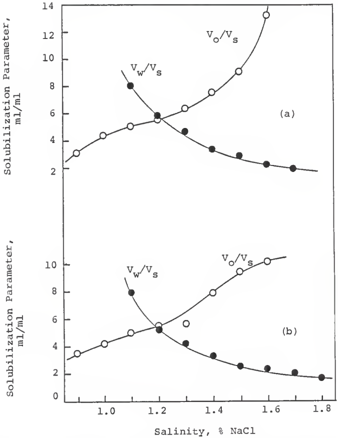

Figure 3.4. Effect of Salinity on Solubilization Parameter for the System 5% TRS 10-410 + 3% IBA + Brine + Oil. WOR = 1 and oil (EACN = 12) is (a) a mixture of nonane + pentadecane or (b) octane + hexadecane.

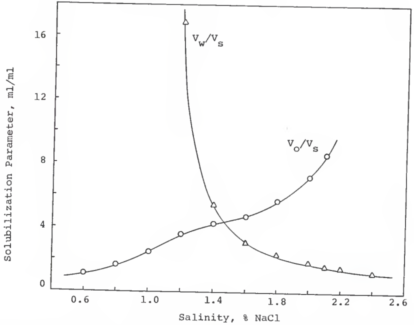

Figure 3.5. Effect of Salinity on Solubilization Parameter for the System 5%TRS 10-410 + 3% IBA + Brine + Tetradecane (WOR = 1).

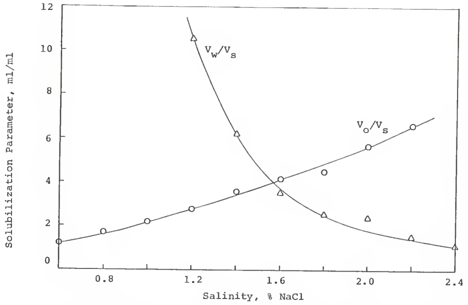

Figure 3.6. Effect of Salinity on Solubilization Parameter for the System 5% TRS 10=410 + 3% IBA + Brine + Oil. WOR = 1 and oil is a mixture of heptane + hexadecane of EACN = 14.

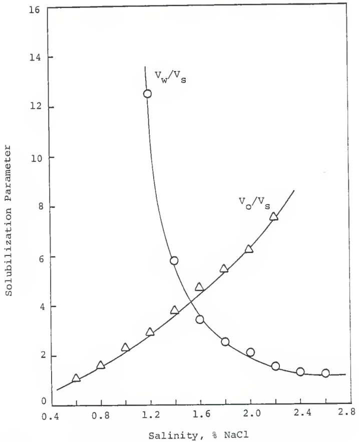

Figure 3.7. Effect of Salinity on Solubilization Parameter for the System 5% TRS 10=410 + 3% IBA + Brine + Oil. WOR = 1 and oil is a mixture of tridecane + pentadecane of EACN = 14.

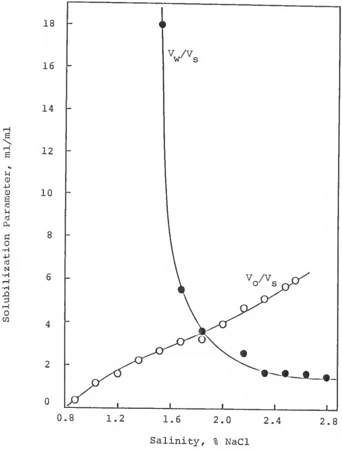

Figure 3.8. Effect of Salinity on Solubilization Parameter for the System 5%TRS 10-410 + 3% IBA + Brine + Hexadecane (WOR = 1).

From these figures, it is also seen that the optimal salinity increased linearly with the EACN. This is in agreement with earlier studies (Salager et al., 1979; Tham and Lorenz, 1981b). Figure 3.9 shows the linearity of optimal salinity as EACN is increased up to 16. This plot can be used for predicting optimal salinity for alkanes. Note that the slope of such plot is specific for a given surfactant, alcohol, and the surfactant to alcohol ratio. This slope will be different if the surfactant, alcohol, or surfactant to alcohol ratio is varied. All systems involving alkanes have optimal salinity identical to that of the pure alkane with the same EACN within the experimental accuracy. Table 3.2 summarizes results of the phase behavior study as single and mixed alkanes were employed as the oil phase. It is also apparent that as the EACN is increased, the solubilization parameter at optimal salinity, a measure of the middle phase volume, decreases while the salinity range of the three-phase region increases. A plot of the range of salinity over which three phases exist versus the EACN can be useful for screening effective surfactant formulations for enhanced oil recovery. Figure 3.10 clearly shows that the surfactant formulation used in this study of 5 wt % TRS 10-410 and 3 wt % isobutyl alcohol produces very narrow ranges of salinity over which such a surfactant is effective when the EACN of oil used is less than 9. Therefore, for example, if a crude oil has an EACN=7, some adjustments have to be made to the formulation

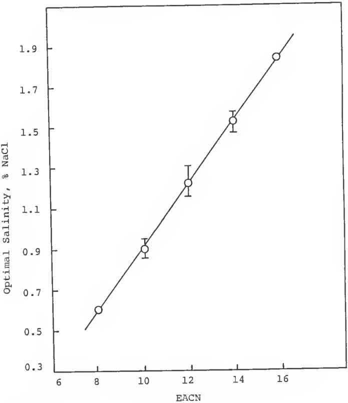

Figure 3.9. Effect of EACN on Optimal Salinity for the System 5% TRS 10-410 + IBA + Brine + Oil. Vertical bar represents the range of optimal salinity values obtained by mixtures of alkanes with identical EACN.

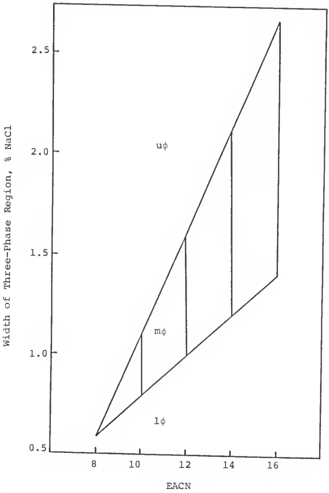

Figure 3.10. Effect of EACN on the Width of the Three-Phase Region for the System 5%TRS 10-410 + 3% IBA + Brine + Oil.

(such as the changes in the structure or concentration of the surfactant and/or alcohol) in order to increase its effective salinity range to insure a successful tertiary oil recovery.

3.4 Phase-Separation Time

An important factor influencing the performance of a surfactant flood is the rate at which an "*in situ* modified surfactant slug" is formed. This slug must solubilize large volumes of brine and oil and enhance the formation and propagation of an oil bank for optimal oil recovery.

The stability of the macroemulsions formed by the surfactant formulation and the *in situ* brine and oil upon contact in the porous medium can influence the efficiency of the oil displacement process. The faster the breakup of a macroemulsion into a middle-phase microemulsion and into excess brine and oil phases, the more efficient the surfactant slug is. The time required for the phase separation to occur has been used as an indication of the rate of coalescence (Baldauf et al., 1982; Vinatieri, 1980). In this work, the time of separation of 80% of the formed phase is taken as the rate of coalescence.

As mentioned in the experimental section, the phase separation in a surfactant/oil/brine system at low salinities (in the l-type microemulsion region) is deduced from the separation time of the oil phase, and at high salinities (in the u-type microemulsion) it is deduced from the separation time of the aqueous phase.

At moderate salinities (in the m-type microemulsion region), the rate of phase separation is inferred from both the oil-phase and the brine-phase separation. Figures 3.11 and 3.12 illustrate respectively, typical data on the oil-phase and the brine-phase separation in the three salinity ranges corresponding to l-, m-, and u-phase microemulsions. In the low-salinity range, after the tubes are removed from the rotator, a relatively stable macroemulsuion is formed which begins to break up, after several hours, at a very slow rate to form an oil phase and a surfactant-rich aqueous phase. The phase separation rate becomes slightly faster as the NaCl concentration is increased. When the low salinity-three phase boundary is passed, the rate of separation of the oil phase accelerates reaching a maximum; then, it slows down as the high salinity-three phase boundary is approached. The brine phase emerges at a slow rate at the low salinity-three phase boundary. Thereafter, the rate accelerates to a maximum value as the system passes the optimal salinity. Then the phase separation slows down as the high salinity-three phase boundary is approached. Figures 3.11 and 3.12 also reveal that at any salinity, the volume fraction-time curve has two portions, a linear part that extends up to a volume fraction of about 0.8 and then a non-linear part. In the three-phase region, the phase-separation process is spontaneous, while in the other

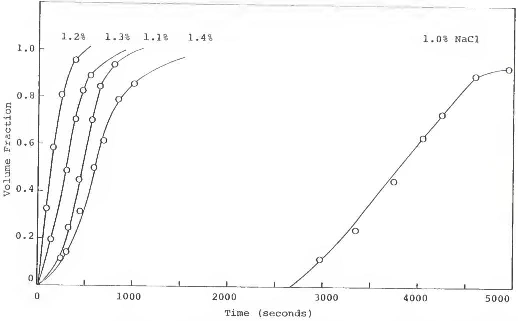

Figure 3.11. Effect of Salinity on Time of Oil Phase Separation for the System 5% TRS 10-410 + 3% IBA + Brine + Oil (WOR = 1). Oil is a mixture of octane + hexadecane of EACN = 12.

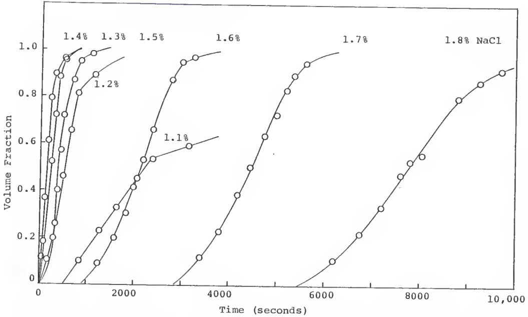

Figure 3.12. Effect of Salinity on Time of Aqueous Phase Separation for the System 5% TRS 10-410 + 3% IBA + Brine + Oil (WOR = 1). Oil is a mixture of octane + hexadecane of EACN = 12.

two salinity regions of lower- and upper-phase microemulsions, there exists an initial time period before which the system remains as a stable macroemulsion. Furthermore, Figure 3.13 clarifies the choice of the time of 80% separation of the formed phase to indicate the rate of coalescence.

The above rate of the phase-separation study was carried out for several systems with single and mixed alkanes employed as the oil phase. The mixed oils are labeled in Table 2.2. Figures 3.14 through 3.24 are plots of the time needed for 80% of the formed oil phase or the brine phase to separate out. This time is called, from now on, the phase-separation time. The oil phase employed was decane, dodecane, tetradecane, hexadecane or binary mixtures of alkanes. The general observation deduced from this study is as follows. At low salinities (1-type microemulsion), the phase-separation time for oil is very long; then, it decreases as the NaCl concentration increases. In the initial part of the three-phase salinity range, the separation rate of the oil phase is faster than that of the brine phase. The separation time of the oil phase reaches a minimum value at a salinity near the optimal salinity, while that of the brine phase goes through a minimum at a salinity just above the optimal salinity, and then, it rises thereafter as the NaCl concentration increases. It is clearly shown that the effect of the mixed alkanes on the

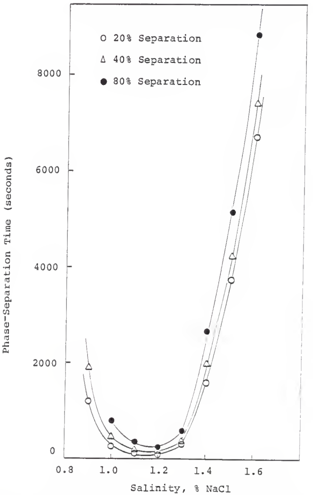

Figure 3.13. The Progress of Oil Phase Separation with Salinity for the System 5% TRS 10-410 + 3% IBA + Brine + Oil (WOR = 1). Oil is a mixture of octane + hexadecane of EACN = 12.

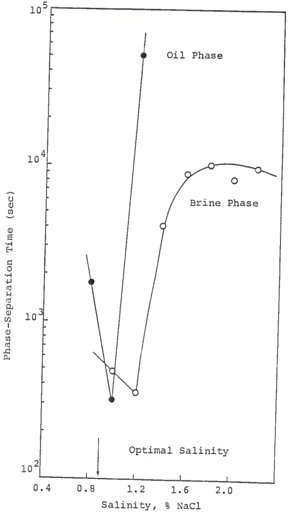

Figure 3.14. Phase-Separation Time as a Function of Salinity for the System: 5%TRS 10-410/3%IBA/Brine/Decane.

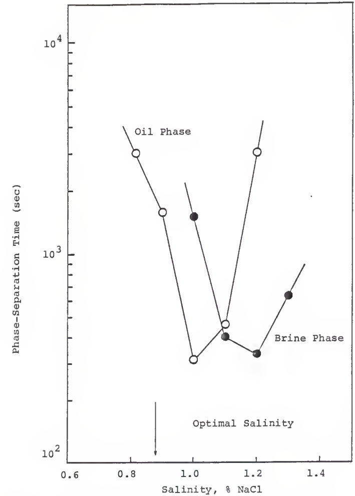

Figure 3.15. Phase-Separation Time as a Function of Salinity for the System 5% TRS 10-410/ 3% IBA/Brine/Oil. Oil is a mixture of hexane + tetradecane of EACN = 10.

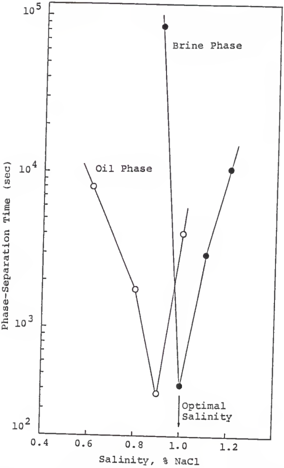

Figure 3.16. Phase-Separation Time as a Function of Salinity for the System 5% TRS 10-410/ 3% IBA/Brine/Oil. Oil is a mixture of octane + dodecane of EACN = 10.

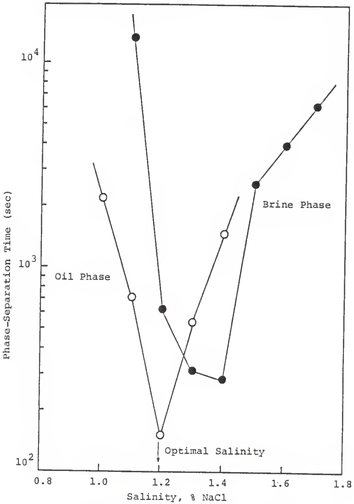

Figure 3.17. Phase-Separation Time as a Function of Salinity for the System: 5%TRS 10-410/ 3%IBA/Brine/Dodecane.

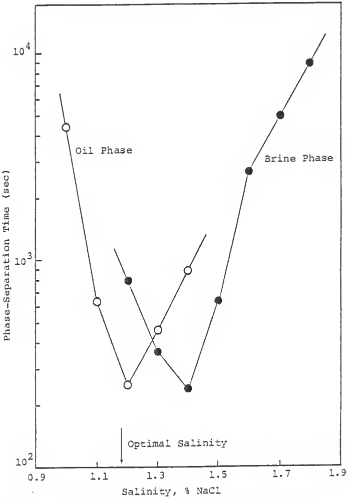

Figure 3.18. Phase-Separation Time as a Function of Salinity for the System 5% TRS 10-410/ 3% IBA/Brine/Oil. Oil is a mixture of decane + tetradecane of EACN = 12.

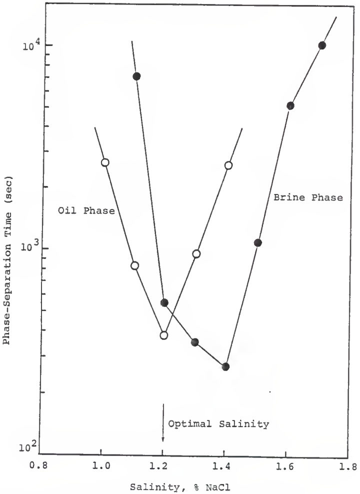

Figure 3.19. Phase-Separation Time as a Function of Salinity for the System 5% TRS 10-410/ 3% IBA/Brine/Oil. Oil is a mixture of nonane + pentadecane of EACN = 12.

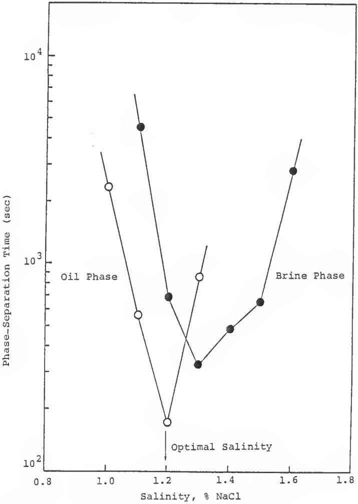

Figure 3.20. Phase-Separation Time as a Function of Salinity for the System 5% TRS 10-410/ 3% IBA/Brine/Oil. Oil is a mixture of octane + hexadecane of EACN = 12.

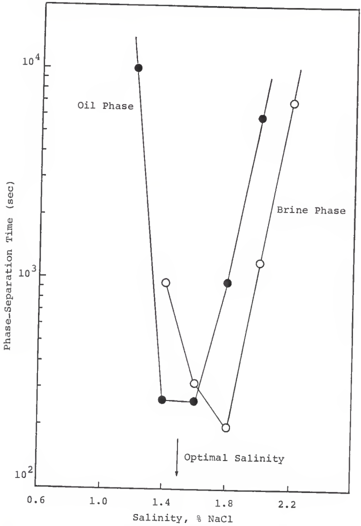

Figure 3.21. Phase-Separation Time as a Function of Salinity for the System: 5%TRS 10-410/ 3%IBA/Brine/Tetradecane.

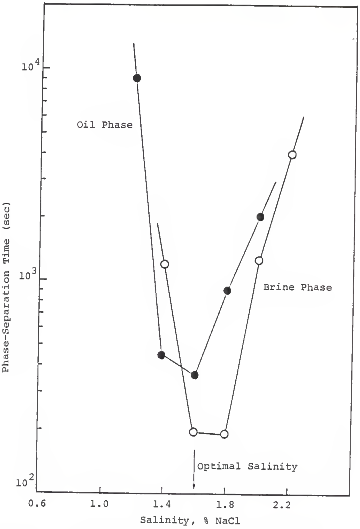

Figure 3.22. Phase-Separation Time as a Function of Salinity for the System 5% TRS 10-410/ 3% IBA/Brine/Oil. Oil is a mixture of heptane + hexadecane of EACN = 14.

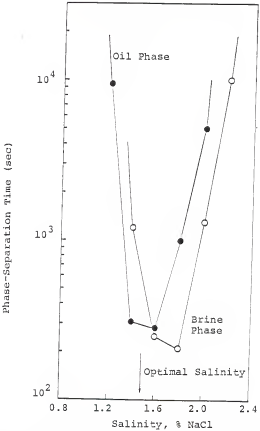

Figure 3.23. Phase-Separation Time as a Function of Salinity for the System 5% TRS 10-410/ 3% IBA/Brine/Oil. Oil is a mixture of tridecane + pentadecane of EACN = 14.

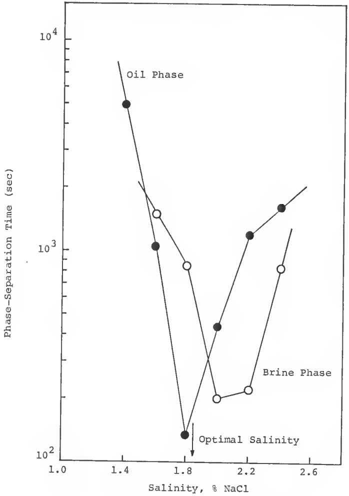

Figure 3.24. Phase-Separation Time as a Function of Salinity for the System: 5%TRS 10-410/ 3%IBA/Brine/Hexadecane.

phase-separation time is identical to that of the single alkane of the same EACN within the experimental accuracy.

A parallel study was conducted substituting a pure surfactant, sodium stearate, for the commercial surfactant. Alkanes were employed as the oil phase. As can be seen in Figure 3.25, 3.26 and 3.27, results identical to those of the systems containing petroleum sulfonate are obtained, i.e., as the oil chain length increases, the optimal salinity increases, the solubilization parameter decreases, and the separation times of the oil and the brine phases go through a minimum close to the optimal salinity.

The rate at which emulsions coalesce depends on many factors, including the interfacial tension between the phases, the difference in density of the phases and the viscosities of the phases (Clayton, 1954; Davies and Rideal, 1961, p. 337). The interfacial tension supplies a driving force for the emulsion to coalesce because a small number of large droplets provides less surface area and less surface free energy than a large number of very small droplets. An interface with high viscosity will hinder the mass transport from one phase to the other. For a surfactant system similar to the ones reported here, it was shown that in the lower-phase microemulsion domain, the interfacial viscosity increases with salinity until it reaches a maximum at the lower boundary of the three-phase system, and it decreases with salinity as the upper-phase boundary is surpassed (Baldauf et al., 1982). Qualitatively, the interfacial

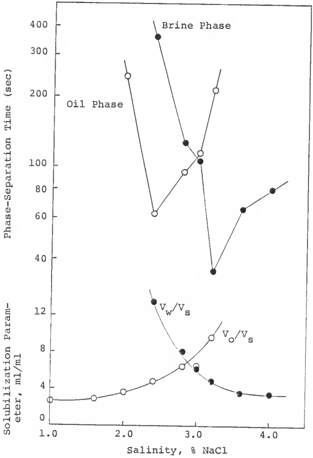

Figure 3.25. Effect of Salinity on Solubilization Parameter and Phase-Separation Time for the System: Sodium Stearate/IBA/Decane/Brine.

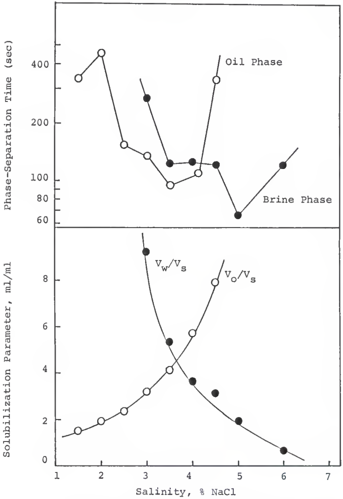

Figure 3.26. Effect of Salinity on Solubilization Parameter and Phase-Separation Time for the System: Sodium Stearate/IBA/Dodecane/Brine.

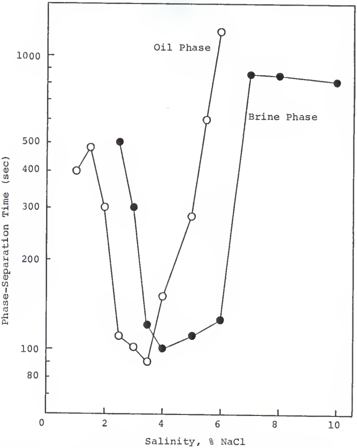

Figure 3.27. Phase-Separation Time as a Function of Salinity for the System: Sodium Stearate/IBA/Hexadecane/Brine.

tension could be correlated to the phase-separation times because a minimum in the interfacial tension coincides with the minimum in the phase-separation time. For high salinities above the upper phase boundary, a collaboration of many other factors along with the salting-out effects may be responsible for the decrease in the phase-separation time (Vinatieri, 1980). Bulk viscosity of the phases involved is shown in Figure 3.28. An abrupt decrease in the aqueous phase is observed as the three-phase salinity domain starts, after which it remains constant. Also, the viscosity of the oil phase increases sharply as the upper phase boundary is crossed. The middle-phase microemulsions exhibit a maximum in viscosity at the optimal salinity. Analogous behavior is observed in the same figure for the density of oil and aqueous phases, respectively. The density of the middle-phase microemulsion decreases linearly with salinity.

3.5 Solubilization of Mixed Alkanes in the Middle-Phase Microemulsions

It is shown in the phase behavior section of this chapter (Figure 3.9) that as the chain length of the oil (EACN) increases, the optimal salinity increases and the concentration of active surfactant in the microemulsion phase at optimal salinity also increases.

For solubilization of mixed alkanes, it is important to single out the factor responsible for the solubilization parameter. Since the alkane chain length influences the

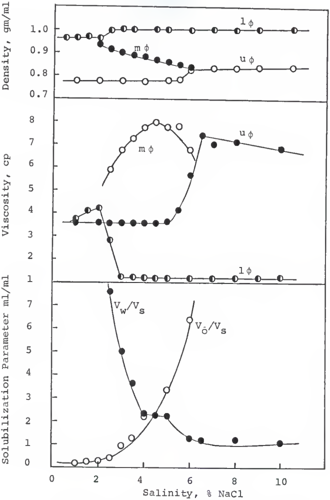

Figure 3.28. Density, Viscosity and Solubilization Parameter Changes with Salinity for the System Sodium Stearate/IBA/Hexadecane/Brine.

solubilization capacity, it is also important to establish whether there is a preference for short chain alkanes in the middle-phase microemulsion as compared to the long chain alkanes. In other words, for example, at a salinity of 1.5% NaCl concentration, pure octane will remain in an upper-phase microemulsion while hexadecane will be solubilized very slightly in a lower-phase microemulsion. When the two alkanes are mixed together in a 1:1 molar ratio, will they be solubilized as one component of EACN? The answer to this question is extremely important for the simulation of crude oil as a single component in surfactant-flooding experiments.

To answer this question, equilibrated systems at different salinities at which three phases coexist were analyzed for their alkane concentration in the excess oil phase using gas chromatography. Various mixtures of alkanes were employed and their concentrations were determined in the excess oil phase for the entire three-phase salinity range.

Results of alkane molar concentrations in the upper phase of a three-phase system at various salinities for several binary combinations of octane and hexadecane, isooctane and hexadecane and hexane and hexadecane are tabulated in Tables 3.3, 3.4 and 3.5, respectively. In these tables, it is clearly shown that for all salinities

Table 3.3. Analysis of Solubilized Mixed Hydrocarbons in the System 5%TRS10-410 + 3%IBA + Brine + Oil (O/W = 1:1(v/v)). Oil is a binary mixture of octane and hexadecane. Octane concentration in the upper phase is reported.

NaCl Concentration (wt.%)	Octane Concentration Mole Fraction		% Difference In Octane Concentration
	Before Mixing	After Mixing	
1.2	0.500	0.510	2.0
1.3	0.500	0.509	1.8
1.4	0.500	0.512	2.4
1.5	0.500	0.512	2.4
1.6	0.500	0.515	2.9
0.8	0.822	0.838	1.9
0.9	0.822	0.836	1.7
0.8	0.888	0.896	0.95
0.9	0.888	0.897	1.1

Table 3.4. Analysis of Solubilized Mixed Hydrocarbons in the System 5%TRS10-410 + 3%IBA + Brine + Oil (O/W = 1:1 v/v). Oil is a binary mixture of hexane and hexadecane. Hexane concentration in the upper phase is reported.

NaCl Concentration (wt.%)	Hexane Concentration Mole Fraction		% Difference In Hexane Concentration
	Before Mixing	After Mixing	
1.0	0.200	0.209	4.5
1.1	0.200	0.208	4.0
1.2	0.200	0.207	3.5
1.3	0.200	0.208	4.0
1.4	0.200	0.208	4.0
1.5	0.200	0.204	2.0
1.6	0.200	0.205	2.5

Table 3.5. Analysis of Solubilized Mixed Hydrocarbons in the System 5%TRS10-410 + 3%IBA + Brine + Oil (O/W = 1:1 v/v). Oil is a binary mixture of isooctane and hexadecane. Isooctane concentration in the upper phase is reported.

NaCl Concentration (wt.%)	Isooctane Concentration Mole Fraction		% Difference In Isooctane Concentration
	Before Mixing	After Mixing	
1.1	0.500	0.505	1.0
1.2	0.500	0.503	0.7
1.3	0.500	0.505	1.0
1.4	0.500	0.502	0.3
0.9	0.75	0.744	-0.8
1.0	0.75	0.745	-0.7
1.1	0.75	0.748	-0.3

the alkane mixture is solubilized as one component. To further illustrate this fact, consider for example Table 3.3.

For this surfactant and alcohol system, the optimal salinity with octane is 0.8% NaCl and 1.85% NaCl with hexadecane. At 1.2% NaCl concentration an upper-phase microemulsion is formed for octane, whereas a lower-phase microemulsion is formed for hexadecane. However, the 1:1 molar mixture of octane and hexadecane (EACN=12) produces a middle-phase microemulsion at 1.2% salinity. Thus, it is evident that the two alkanes act as a single component with an average chain length. Because the solubilization of octane in the middle-phase microemulsion is considerably greater than hexadecane when employed separately, one may expect a preferential partitioning of octane as compared to hexadecane in the middle-phase microemulsion. However, if the mixed alkanes behave as a single component, the molar ratio of alkanes in the middle-phase microemulsion and that in the excess oil phase should remain the same. This indeed was experimentally observed (Tables 3.3 through 3.5). Within the experimental accuracy, the ratio of the two alkanes in the excess oil phase remained the same as that of the initial ratio of the mixed alkanes.

3.6 Summary

The following are conclusions from the results presented in this chapter:

1. Single and mixed alkanes of the same equivalent alkane carbon number produce systems with identical phase and coalescence behavior when used as the oil component in surfactant systems containing TRS 10-410, isobutanol, brine and oil.
2. As the equivalent alkane carbon number of oil in a surfactant system increases, the optimal salinity increases linearly, the solubilization parameter at optimal salinity decreases, and the salinity range of the three-phase region increases. The salinity range

of the three-phase region vanishes when the EACN is ≤ 8.

3. The effect of salinity on the separation of the phases forming in a surfactant system is as follows. The oil phase separates at a very slow rate at low salinity. As the salinity is increased, the rate accelerates rapidly reaching a maximum at or near the optimal salinity. Then it decreases as the salinity is further increased beyond the optimal salinity. The brine phase emerges at a slow rate when the system first begins to exhibit three phases. Then the rate of separation accelerates with salinity reaching a maximum as the optimal salinity is passed. Thereafter, the rate slows down as the high salinity-three phase boundary is approached.
4. When binary mixtures of alkanes represent the oil component of the system, the concentration of each of the two alkanes remains unchanged after solubilization takes place. The mixture behaves as a single component represented by the EACN of the mixture.

CHAPTER IV

OIL DISPLACEMENT EFFICIENCY AND THE COMPOSITIONAL CHANGES INDUCED BY FLOW THROUGH POROUS MEDIA

4.1 Introduction

The movement of fluids through porous media is governed by the empirical Darcy's law (Craft and Hawkins, 1959) which states that the velocity of a homogeneous fluid in a porous medium is proportional to the pressure gradient, and inversely proportional to the fluid viscosity, or

$$\frac{Q}{A} = v = - \frac{k}{\mu} \frac{\Delta p}{\Delta x} \qquad (4.1)$$

where

Q is the volumetric flow rate in cm^3/sec,

A is the apparent or total cross-sectional area of the rock in cm^2,

μ is the fluid viscosity in centipoise,

v is the apparent velocity in cm/sec,

$\frac{\Delta p}{\Delta x}$ is the pressure gradient in atm/cm taken in the same direction as v and Q, and

k is the permeability of the rock expressed in Darcy units.

For multifluid immiscible flow of incompressible fluids in an isotropic porous medium with no gravity, Darcy's law is assumed valid for each flowing fluid and thus the equations of change are written for each fluid and connected using capillary pressure and saturation of the various fluids as follows (Greenkorn, 1983):

$$\underline{v}_i = -\frac{k_i}{\mu_i}\underline{\nabla}\, p_i \tag{4.2}$$

and

$$\phi = \frac{\partial S_i}{\partial t} = -(\underline{\nabla}\cdot\underline{v}_i) \tag{4.3}$$

where $$\sum_{i=1}^{N} S_i = 1 \tag{4.4}$$

and $$p_c = p_n - p_w$$

where $\underline{v}_i$, μ_i, p_i, k_i and S_i are the respective apparent seepage velocity vector, viscosity, pressure, effective permeability and fractional saturation of fluid i. Also, ϕ is the porosity, N is the total number of fluids, p_c is the capillary pressure where n and w stand for nonwetting and wetting fluids respectively, t is time and $\underline{\nabla}$ is the "del" operator.

Note that the effective permeability depends on the pore structure and on the fluid present. Where two fluids like oil and water flow, their relative rates of flow are determined by their relative viscosities and their relative permeabilities where the relative permeability is the ratio of effective permeability to the absolute permeability.

A typical plot of oil and water relative permeabilities for a specific rock is shown in Figure 4.1. At 15% oil saturation, the relative permeability of oil is zero. This value of oil saturation is called the residual saturation, the value below which the saturation cannot be reduced in an oil-water system. It is also seen from the figure that the sum of relative permeabilities is always less than unity, which has been attributed to tortuosity of the flow paths and to the decrease in the cross-sectional area due to multiphase flow (Craft and Hawkins, 1959; Langnes et al., 1972).

Chemical and/or thermal treatment of oil reservoirs to increase the production of crude oil, after the secondary oil recovery process becomes uneconomical, is referred to as tertiary oil recovery. However, only the use of surfactant slugs for enhanced oil recovery will be discussed in the present study.

After the water flooding (i.e., secondary oil recovery), between 50 and 70% of the oil remains in the petroleum reservoirs as oil ganglia. The formation of such oil ganglia during water flooding depends on oil-water interfacial tension, pressure gradient (Stegemeier, 1974), pore geometry (Dullien et al., 1972) and perhaps, on surface rheology of the interfacial film (Kimbler et al., 1966). When water penetrates the porous rock, it causes rupture of

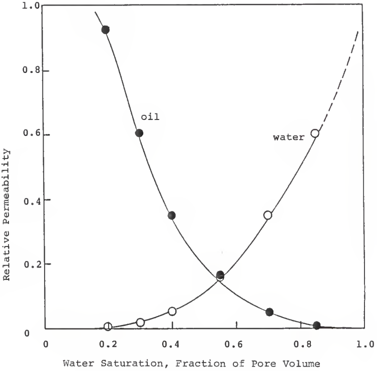

Figure 4.1. Water-Oil Relative Permeability Curves.

the continuous oil filaments extending over a few pores, and thus isolates oil ganglia from each other. Hence, the goal of a tertiary oil recovery technique is to displace the trapped oil ganglia and to form a continuous flowing oil bank by the coalescence of the oil ganglia (Reed and Healy, 1977).

A simple model of the trapped oil ganglion is shown in Figure 4.2. Using Laplace Equation, it follows that the pressure difference, Δp, across the oil droplet is written approximately as (Reed and Healy, 1977)

$$\Delta p = 2\gamma \left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

where, γ is the interfacial tension between oil and water in dynes/cm and r_1 and r_2 are radii of curvature of the droplet in centimeters. The following assumptions were used in obtaining the equation of the pressure difference across the oil droplet:

1) The rock is water-wet.
2) Advancing and receding contact angles are zero.
3) Interfacial tension is the same at all oil-water surfaces.
4) Interfaces are spherical in shape.

Two kinds of forces control the mobilization of trapped oil ganglia, viscous and capillary forces (Leverett et al., 1942; Melrose and Brandner, 1974). These two forces are

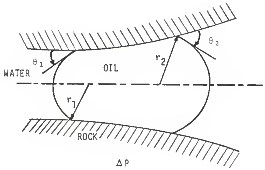

Figure 4.2. Trapped Oil Ganglion.

coupled in a dimensionless group called the capillary number, N_c, (Abrams, 1975; Catchpole and Fulford, 1966; Foster, 1973; LeFebvre du Prey, 1966). Capillary number is the ratio of the viscous forces to capillary forces:

$$N_c = \frac{v\mu}{\phi\gamma}$$

where

v is the flow velocity in cm/sec,

μ is the viscosity of displacing fluid in centipoise,

ϕ is the porosity of porous medium, and

γ is the oil/water interfacial tension in dyne/cm.

In order to overcome the capillary forces, which prevent the movement of the oil droplet, the pressure drop across that droplet has to be exceeded (Gardescu, 1930; Taber, 1969). If typical values (Reed and Healy, 1977) of γ, r_1, r_2, and a are taken as 30 dynes/cm, 9×10^{-4} cm, 4×10^{-3} cm and 4×10^{-2} cm respectively, where a is the length of the drop, they yield a pressure gradient of 128 atm/m (571 psi/ft). At least such a pressure gradient must be developed in order to displace the oil ganglion. Note that the practically achieved value for the pressure gradient in petroleum reservoirs is about 1-2 psi/ft (Healy et al., 1975; Parsons, 1974).

These typical values reflect an N_c value of 10^{-6}. Therefore, it is clear that the pressure gradient across the oil drop has to be reduced by at least two or three orders of magnitude, and subsequently the capillary number has to be increased by the same order so that oil ganglia could be mobilized (Bansal and Shah, 1977).

The flow velocity and the viscosity of the displacing fluid can be changed only within narrow limits under reservoir conditions, therefore, the possibility of reducing the interfacial tension by three or four orders of magnitude by the use of suitable surfactant formulations becomes the only feasible approach for oil displacement. Hence, the achievement of ultralow interfacial tension should lead to successful enhanced oil recovery.

Extensive studies by researchers in this field show that interfacial tension between oil and water can actually be lowered from 30 to 0.001 dyne/cm by adding a proper surfactant (Chiang, 1979; Hsieh and Shah, 1977; Morgan et al., 1979). The role of ultralow interfacial tension in promoting the mobilization of oil ganglia in porous media is sketched in Figure 4.3.

Surfactant systems for tertiary oil recovery commonly involve at least five components: oil, water, surfactant, cosurfactant and electrolyte. Several studies have shown that most of the oil is displaced by virtue of immiscible flooding when surfactant solution contacts the residual oil and allows for the in situ generation of the microemulsion (Boneau and Clampitt, 1977; Glinsmann, 1978; Healy et al., 1975).

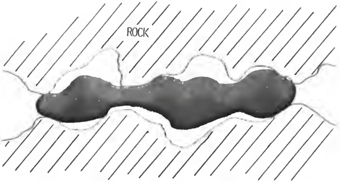

Figure 4.3. Schematic Diagram Showing the Role of Low Interfacial Tension in the Surfactant Flooding Process.

Some of the important variables of surfactant formulations are oil, salinity, and structure and concentration of surfactant and cosurfactant. These variables have direct influence on the interfacial tension between oil and water and also on the phase behavior of a surfactant system. It has been shown that ultralow interfacial tension can be attained when a middle-phase microemulsion is formed in equilibrium with excess oil and brine phases (Reed and Healy, 1977). Thus, a potential surfactant formulation for a successful enhanced oil recovery should be capable of forming three phases of which the middle phase must solubilize large amounts of oil and brine. It has been shown on theoretical grounds that the interfacial tension is inversely proportional to the solubilization parameter (Huh, 1979).

In the present chapter, oil displacement efficiency is measured for several surfactant formulations. The effect of alcohol structure on oil displacement efficiency is delineated. The equivalent alkane carbon number concept is tested for oil displacement through porous media. Surfactant and alcohol concentration in the effluent fluids is monitored to propose criteria for a better efficiency of oil displacement.

4.2 Experimental

A commercial petroleum sulfonate, TRS 10-410 (Witco Chemical Company), which has an average molecular weight of

418 and consists of 61% active material was used as received. Isopropyl alcohol (IPA), n-butyl alcohol (NBA), isobutyl alcohol (IBA), tertiary amyl alcohol (TAA) and isoamyl alcohol (IAA) were employed as cosurfactants (all of 99% purity from Fisher Scientific Company, except isoamyl alcohol from J.T. Baker Chemical Co.; Phillipsburg, N.Y.). Alkanes of > 99% purity were employed in the present study. Sodium chloride (99% from Fisher Scientific Company) was dissolved in deionized distilled water to prepare brine solutions. Pusher-1000^{TM}, a partially hydrolyzed polyacrylamide, was employed to prepare the polymer solutions. Sandpacks with a dimension of 30 cm length and 2.5 cm diameter were used as the porous medium. In a typical tertiary oil recovery experiment, the sandpack was preconditioned by saturating it with CO_2 to displace air, then flooding it with brine up to 10 pore volumes during which the permeability was measured as shown in Figure 4.4. The core was then flooded with oil to the irreducible brine content (about 19% pore volume), followed by brine flooding to the irreducible oil content (approximately 23% pore volume). A surfactant slug (10% pore volume) containing 5% (wt) surfactant and 3% (wt) alcohol was then injected followed by (1 pore volume) polymer solution (1500 ppm) and subsequently by drive brine. The salinity of surfactant slug and polymer solution was the same as that of brine used throughout the run. The linear displacement velocity used

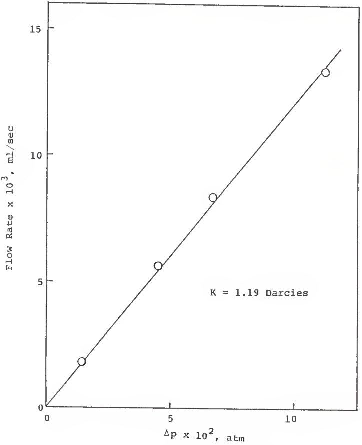

Figure 4.4. Measurement of Absolute Permeability of Sandpacks.

in the entire experiment was 2 ft/day. Oil displacement efficiency is calculated as

$$\frac{\text{volume of oil recovered after secondary recovery}}{\text{volume of residual oil}} \times 100\,.$$

All tests were performed at room temperature (24° C). Surfactant concentration in the effluent fluid was determined by the two-phase dye titration method mentioned in Section 2.2, while alcohol concentration and alkane concentration were determined by a Perkin Elmer 900 gas chromatograph. Alcohol concentration was calculated by averaging the concentration values in the oil and brine phases over the total volume. Interfacial tension was measured by the Spinning Drop Interfacial Tensiometer. Figure 4.5 shows the apparatus for the oil displacement studies.

4.3 Oil Displacement, Optimal Salinity and EACN

In this section the validity of the following two concepts are explored. The first is that maximal oil recovery would be obtained at optimal salinity of the surfactant formulation. The second is that oil displacement efficiency attained for a mixture of alkanes would be equal to that of a pure alkane of the same equivalent alkane carbon number.

The surfactant slug used for this study consisted of 5 wt % TRS 10-410 and 3% isobutyl alcohol in brine. The salinities of formation brine, brine for secondary flooding, surfactant slug and of the polymer solution were made equal.

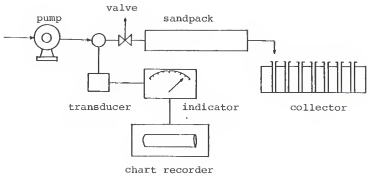

Figure 4.5. Oil Displacement Apparatus.

Dodecane and two mixtures of 1:1 molar ratio of decane and tetradecane, and octane and hexadecane were employed as oil in displacement studies.

As shown in Figure 4.6, maximal oil recovery is obtained when the NaCl concentration is 1.2% (optimal salinity). The salinity for maximal oil recovery correlated well with the optimal salinity obtained from the solubilization and the phase-separation time results (see Sections 3.3 and 3.4). This finding of maximal oil recovery at optimal salinity is consistent with earlier work (Chiang, 1979; Chou, 1980).

Figure 4.6 also reveals that the oil displacement efficiency produced is the same for single or mixed alkanes of an equivalent alkane carbon number. It should be noted that the molar composition of alkanes (obtained by G.L.C.) collected in the effluent fluid was the same as that of the original mixture. This proves again that the oil mixture flows in the porous medium as a single component.

4.4 Efficiency of Oil Displacement in Porous Media

4.4.1 The Influence of the Structure of Alcohol on Microemulsion Phase Behavior and Oil Displacement Efficiency

A short chain alcohol is an essential component of a microemulsion or a surfactant formulation for enhanced oil recovery. It is often referred to as a cosolvent or a cosurfactant (Dominguez et al., 1979; Gogarty and Tosch,

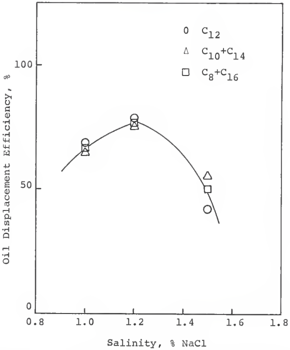

Figure 4.6. Effect of Salinity on Oil Displacement Efficiency.

1968; Healy et al., 1976; Puerto and Gale, 1977). Alcohol can stabilize a microemulsion and adjust its viscosity and fluidity. Alcohol also influences the interfacial tension and phase behavior of microemulsion formulations (Baviere et al., 1981).

In this section, oil displacement tests were conducted for a surfactant solution containing 5% (by weight) TRS 10-410, a petroleum sulfonate, 3% alcohol and brine. The salinity of the surfactant solution chosen was the optimal salinity of the surfactant/alcohol/dodecane/brine system. The structure of alcohol was used as the primary variable.

Oil displacement efficiency along with interfacial tension data are shown in Table 4.1 for surfactant slugs that contained isopropanol, n-butanol, tertiary amyl alcohol, isoamyl alcohol or isobutanol. It is evident that high oil recovery values are obtained with the use of isobutanol, n-butanol and tertiary amyl alcohol, while poor oil recovery is obtained with isopropanol and isoamyl alcohol. Before these results are discussed, phase behavior data will be presented.

The solubilization parameter is plotted as a function of salinity for the systems containing isopropanol, n-butanol, isobutanol, isoamyl alcohol and tertiary amyl alcohol as shown in Figures 4.7, 4.8, 4.9 and 4.10, respectively. The important features of these phase diagrams, i.e., the salinity width of the three-phase region and the

Table 4.1. The Effect of Various Alcohols on the IFT Between Excess Oil (Dodecane) and Excess Brine, and on Oil Displacement Efficiency and Surfactant Retention in Porous Media.

Alcohol	Salinity %NaCl	Optimal Salinity %NaCl	IFT Dyne/cm	Oil Displacement Efficiency	%Surfactant Retention
Isopropanol	2.5	2.5	0.004	38.5	87
n-Butanol	1.15	1.15	0.013	85.1	34
Tert-Amyl Alcohol	1.55	1.55	0.006	82.2	40
Isoamyl Alcohol	0.32	0.32	0.008	31.9	74
Isobutanol	1.0	1.2		68.0	38
Isobutanol	1.2	1.2	.005	78.3	49
Isobutanol	1.5	1.2		41.9	55
Isobutanol*	1.0	1.2		64.8	42
Isobutanol*	1.2	1.2		75.2	54
Isobutanol*	1.5	1.2		55.5	50
Isobutanol**	1.2	1.2		76.4	47

*Oil used: 12C (See Table 2.2).

**Oil Used: 12E (See Table 2.2).

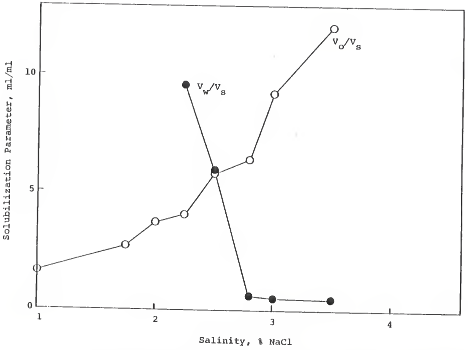

Figure 4.7. Effect of Salinity on Solubilization Parameter for the System TRS 10-410/IPA/Brine/Dodecane.

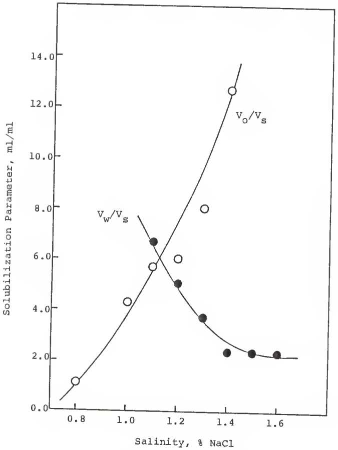

Figure 4.8. Effect of Salinity on Solubilization Parameter for the System: TRS 10-410/n-Butanol/Brine/Dodecane.

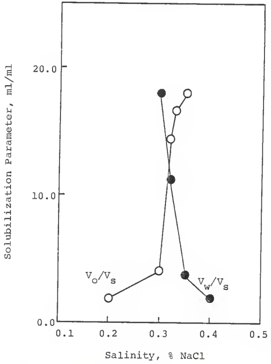

Figure 4.9. Effect of Salinity on Solubilization Parameter for the System: TRS 10-410/Isoamyl Alcohol/Brine/Dodecane.

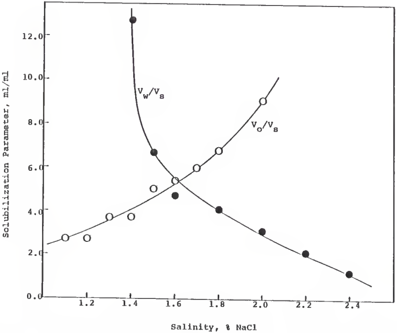

Figure 4.10. Effect of Salinity on Solubilization Parameter for the System: TRS 10-410/Tert-amyl Alcohol/Brine/Dodecane.

solubilization parameter at optimal salinity are summarized in Table 4.2.

The solubilization parameter for the system containing isoamyl alcohol was the highest, but it exhibits a very narrow range of the three-phase region. Also, its middle phase microemulsion is turbid rather than transparent or translucent. It is noteworthy to report that the surfactant-rich phase of the system containing isopropanol appeared to be two distinct phases.

Willhite et al. (1980), from their study of oil displacement by a microemulsion system, proposed a mechanism for displacement of the oil and water bank. They proposed that macroemulsions were generated in situ by mixing of fluids and shear in porous media. These forces, combined with low interfacial tensions, create and/or maintain a new interfacial area. Both oil and water can be displaced by the macroemulsion through a combination of miscibility and low apparent interfacial tension. It has also been proposed by Larson et al. (1982) that changes in the compositions of the fluid phases due to the presence of chemical additives are one of two mechanisms by which postwater-flood residual oil can be recovered. Those changes in compositions of the aqueous and oleic phases can be described approximately, at least, by means of pseudoternary equilibrium phase diagrams.

When a surfactant slug is injected into the porous medium, its composition changes. Moreover, as can be observed from measurements of the surfactant and alcohol

Table 4.2. The Effect of Various Alcohols on Solubilization Parameter at Optimal Salinity (Opt. Sal.) and Salinity Width of the Three-Phase Region for the System TRS 10-410/Alcohol/Brine/Dodecane.

Alcohol	Solubilization Parameter at Opt. Sal., ml/ml	Range of Salinity Width of 3-Phase Region, % NaCl	Salinity Width of 3-Phase Region, % NaCl	Oil Displacement Efficiency, %
Isopropanol	5.8	2.25 - 4.0	1.75	38.5
n-Butanol	6.0	1.1 - 1.4	0.3	85.1
Isobutanol	5.9	1.0 - 1.5	0.5	78.3
Tert-amyl alcohol	5.4	1.4 - 2.0	0.6	82.2
Isoamyl alcohol	12.2	0.30 - 0.35	0.05	31.9

concentrations in the effluent fluids, the surfactant-to-alcohol ratio is also changed as the slug travels through the porous medium. The following section reports studies on changes in the surfactant and alcohol concentrations in the produced fluids.

4.4.2 Determination of Alcohol and Surfactant Concentration in the Produced Fluids

Systems containing isobutanol. As mentioned in Section 4.3, three salinities within the Type III microemulsion region were used, i.e., below, at and above optimal salinity (1.0%, 1.2%, and 1.5% NaCl, respectively). Surfactant and alcohol concentrations in the produced fluids (oil and brine) as the surfactant slug travels through the porous medium are shown in Figures 4.11, 4.12 and 4.13, respectively. Figures 4.14 and 4.15 show alcohol and active surfactant concentrations in the effluent fluid at 1.2% NaCl when 1:1 moles of $C_{10} + C_{14}$ and $C_8 + C_{16}$ were employed, respectively. Note that the sample collection of effluent fluids starts just at the beginning of the surfactant slug injection. From these figures the following is observed:

a) For 1% NaCl systems (Fig. 4.11), oil breaks through at 0.55 pore volume (PV) after the surfactant slug injection, while the surfactant and alcohol breakthrough occurs simultaneously at 0.8 PV. Both surfactant and alcohol concentrations reach maximum at the same PV (1.06)

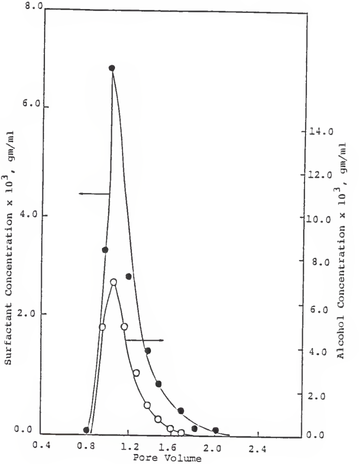

Figure 4.11. Surfactant and Alcohol Concentrations in the Effluent Fluids. Surfactant slug is TRS 10-410 + IBA in 1.0% NaCl solution.

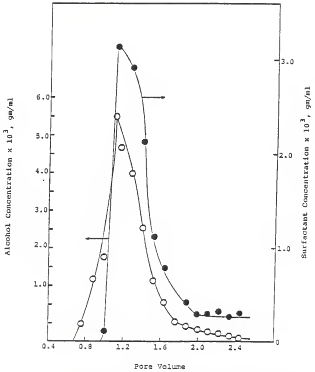

Figure 4.12. Surfactant and Alcohol Concentrations in the Effluent Fluids. Surfactant slug is TRS 10-410/IBA in 1.2% NaCl solution.

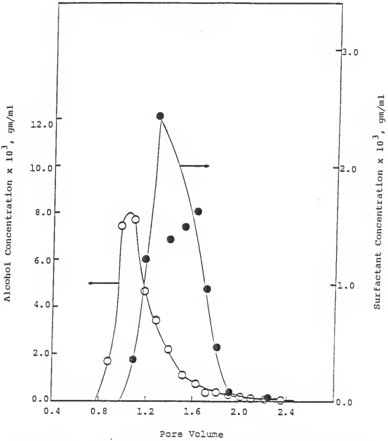

Figure 4.13. Surfactant and Alcohol Concentrations in the Effluent Fluids. Surfactant slug is TRS 10-410/IBA/1.5% NaCl solution.

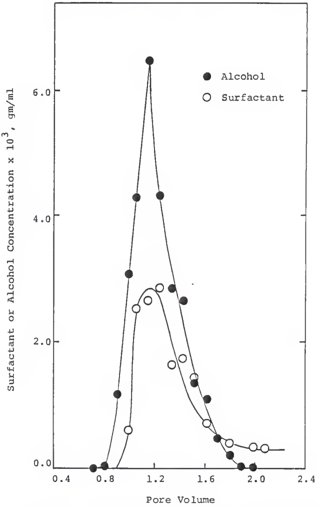

Figure 4.14. Surfactant and Alcohol Concentrations in the Effluent Fluid. Surfactant slug is TRS 10-410/IBA in brine at optimal salinity (1.2% NaCl) of formulation, and oil is a mixture of decane + tetradecane of EACN = 12.

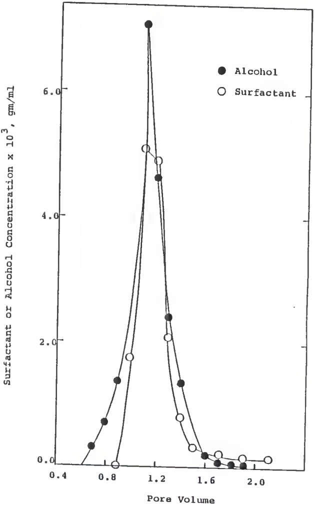

Figure 4.15. Surfactant and Alcohol Concentrations in the Effluent Fluid. Surfactant slug is TRS 10-410/IBA in brine at optimal salinity of formulation, and oil is a mixture of octane + hexadecane of EACN = 12.

at which the active surfactant-to-alcohol ratio is 0.96, which is very close to that of the injected slug of 1.00. Also, as the surfactant and alcohol move inside the porous medium, the surfactant-to-alcohol ratio (S/A) is not very far from that of the injected slug.

b) For 1.2% NaCl systems (optimal salinity), the oil breakthrough occurs at 0.67 PV after surfactant slug injection, whereas the surfactant appears at 0.90 PV and alcohol at 0.65 PV (Fig. 4.12). Both surfactant and alcohol concentrations reach a maximum at 1.1 PV at which the active surfactant-to-alcohol ratio is 0.52. This ratio increases gradually to 0.9 as more fluids are collected.

c) For 1.5% NaCl systems (Fig. 4.13), the oil breakthrough occurs at 0.75 PV, alcohol at 0.75 PV and surfactant at 0.95 PV after the injected slug. The alcohol concentration curve goes through a maximum at 1.0 PV, and the surfactant concentration curve at 1.28 PV. The S/A ratio at the surfactant concentration peak is 0.7.

d) The surfactant concentration peak for the 1% NaCl system is very high compared to those of the other two salinities (1.2 and 1.5% NaCl).

e) Surfactant and alcohol migration into the oil phase is significant at and above the optimal salinity.

f) No correlation is observed between oil recovery and surfactant loss due to salinity changes (See Table 4.1).

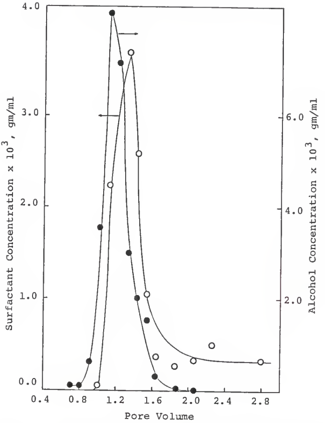

Figure 4.16. Surfactant and Alcohol Concentrations in the Effluent Fluid. Surfactant slug is TRS 10-410/TAA in brine at optimal salinity of formulation.

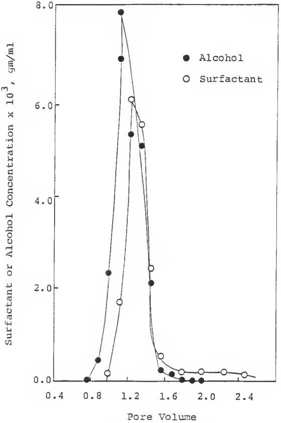

Figure 4.17. Surfactant and Alcohol Concentrations in the Effluent Fluid. Surfactant slug is TRS 10-410/NBA in brine at optimal salinity of formulation.

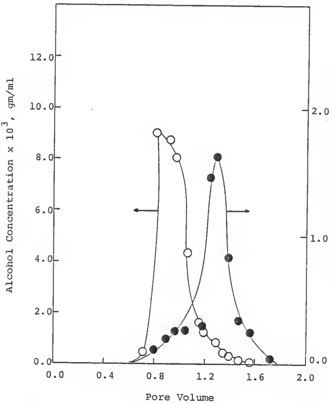

Figure 4.18. Surfactant and Alcohol Concentrations in the Effluent Fluids. Surfactant slug is TRS 10-410/IPA in brine at optimal salinity of formulation.

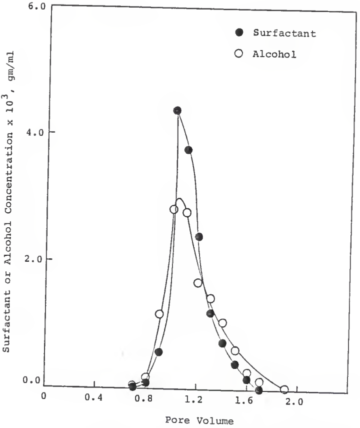

Figure 4.19. Surfactant and Alcohol Concentrations in the Effluent Fluids. Surfactant slug is TRS 10-410/IAA in brine at optimal salinity of formulation.

g) Poor oil recovery for the 1.5% NaCl system could be due to the striking changes in the S/A ratio *in situ*, which could have altered the interfacial tension and phase behavior in the porous medium.

h) Alcohol and surfactant concentrations for the mixed alkanes are similar to that of dodecane at optimal salinity.

Systems containing TAA, NBA, IPA and IAA. Oil displacement efficiency at the optimal salinity of each of the systems containing TAA, nBA, IPA and IAA was determined. Surfactant and alcohol concentrations of the produced fluids are shown in Figures 4.16 through 4.19 for the above mentioned systems, respectively. TAA and NBA curves reveal information similar to those mentioned for the IBA system at optimal salinity. For the curves of IPA and IAA, considerable differences are observed. In the IPA system, alcohol breakthrough occurs at 0.6 PV and alcohol concentration reaches a maximum at 0.81 PV, indicating that rapid diffusion of isopropanol into brine has taken place (chromatographic separation). The S/A ratio is very low throughout the recovery process. Huge surfactant loss (87%) was experienced. An explanation of the process that took place in this system is as follows:

As the surfactant slug contacted the connate brine, isopropanol diffused preferentially into the brine, changing the S/A ratio in the slug and forming a stable emulsion which failed to mobilize oil blobs or to form an oil bank.

(The following section discusses the importance of the S/A ratio and its effect on oil and brine solubilization.) Hence, though the starting formulation was at optimum conditions, it was shifted swiftly into "undesired" conditions once it contacted the in situ brine due to the infinite solubility of isopropanol in brine. Moreover, phase-separation time measurements reveal that the isopropanol system took several hours before separating into three phases at optimal salinity. Therefore, the formation of the middle-phase microemulsion did not occur in situ and subsequently it resulted in very poor oil displacement efficiency.

It is important to note that the isoamyl alcohol system has a very narrow range of salinity within which three phases coexist. Thus, a small change in the S/A ratio or in the surfactant concentration would lead to a shift to a two-phase system of high interfacial tension. In addition, the three phases took several hours to form. The slug traveled through the porous medium but was ineffective to solubilize or mobilize significant amounts of oil.

For the formulations that gave good oil recovery, the following common factors besides ultralow IFT were observed

Wide range of three-phase salinity. This factor ensures the in situ formation of the middle phase microemulsion (at least near the optimum conditions). Such a microemulsion provides low interfacial tension between oil and brine and promotes the mobilization of discrete oil ganglia into an oil bank.

High solubilization parameter. A formulation that solubilizes large amounts of oil leads to good oil recovery (Barakat et al., 1983).

Rapid separation of the emulsion into three phases. This factor is very important because a rapid phase separation enhances the early formation of an oil bank and minimizes the compositional changes of the surfactant slug that would take place before the oil bank formation. These compositional changes could alter the phase behavior of the surfactant system into an "undesired" one (for example, a case of high interfacial tension or poor solubilization).

Relatively low partitioning of alcohol in brine. High alcohol solubility in brine will result in excessive partitioning of alcohol into the brine phase. This will change the surfactant-to-alcohol ratio of the surfactant slug and may lead to a very different phase diagram, and stable macroemulsions.

4.5 Effect of Cosurfactant-to-Surfactant Ratio on Solubilization of Oil and Brine

In this section, results of the effect of the alcohol to surfactant ratio on the solubilization parameter of a surfactant formulation are presented. Brine of 1.2% NaCl, dodecane, TRS 10-410 petroleum sulfonate and isobutanol were used for this study. The oil and brine solubilization data was obtained by two experimental methods. In the first experiment, small amounts of equal volume of oil and brine were added gradually to a surfactant-alcohol mixture of constant ratio until the system became turbid. In the second experiment, the oil-to-surfactant ratio is also fixed. Maximum solubilization refers to maximum uptake of brine by the mixture of surfactant, alcohol, and oil.

Figure 4.20 clearly indicates that the maximum oil and brine (oil:brine is 1:1 by volume) solubilization is achieved in a narrow range of surfactant to alcohol ratio. Also, the solubilization parameter is quite large. This finding is again supported by the slightly different second experiment as shown in Figure 4.21 where significant brine uptake was obtained only at a specific alcohol-to-surfactant ratio of 0.15. Ratios of alcohol to surfactant below and above 0.15 gave poor brine uptake.

Brine solubilization is highly dependent on the amount of oil present. As can be seen in Figure 4.21, a maximum was reached at a volume of 3.75 ml of dodecane per gram TRS 10-410. Finally, brine solubility in a mixture of isobutanol and TRS 10-410 goes through a maximum at a ratio of 0.3 (gram alcohol/gram surfactant). These results support the previous explanation (Section 4.4) that changes in the alcohol/surfactant ratio in the porous medium can influence the solubilization parameter and hence the interfacial tension. Subsequently, this could lead to poor oil displacement efficiency.

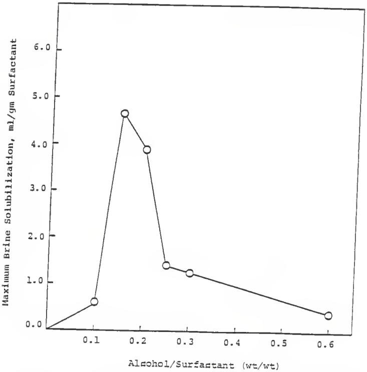

Figure 4.20. Effect of Alcohol-to-Surfactant Ratio on Maximum Brine Solubilization for the System TRS 10-410 + IBA + Equal Volumes of 1.2% NaCl Brine and Dodecane.

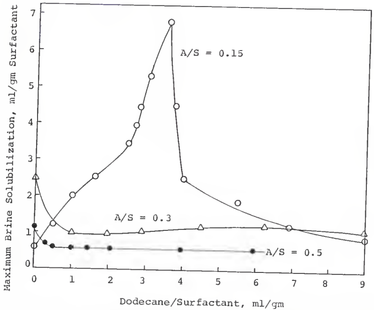

Figure 4.21. Effect of Alcohol/Surfactant Ratio on Maximum Brine Solubilization for the System TRS 10-410 + IBA + Dodecane + 1.2% NaCl Brine.

4.6 Summary

In this chapter the transport of fluids through porous media and the importance of achieving a certain capillary number in order to obtain better oil displacement efficiency were discussed. The effect of salinity and cosurfactant structure on oil displacement efficiency was determined. The equivalent alkane was tested for oil displacement efficiency. The effect of the cosurfactant-to-surfactant ratio on the solubilization capacity was examined.

The following conclusions were drawn from the studies in this chapter:

1. Maximum oil recovery was obtained at the optimal salinity of a surfactant formulation, but no correlation was found between oil displacement efficiency and surfactant retention in sandpacks.
2. The use of a surfactant formulation of TRS 10-410 petroleum sulfonate and isobutanol blend to recover pure and mixed alkanes confirmed the validity of the equivalent alkane carbon number concept.
3. Surfactant systems with a wide salinity range of the three-phase domain, a large solubilization parameter and a short phase separation time provided better oil recovery.
4. Surfactant systems with a very narrow salinity range of the three-phase region or having an alcohol of high partitioning in brine yielded poor oil displacement and high surfactant retention in sandpacks.

5. Analysis of alcohol and surfactant in the effluent fluid assisted in predicting the effectiveness of a surfactant formulation for tertiary oil recovery.
6. The brine and/or oil solubilization capacity of a mixture of surfactant and alcohol depends highly on the surfactant-to-alcohol ratio.

CHAPTER V

ALCOHOL PARTITIONING IN INTERFACE AND ADJACENT BULK PHASES IN MICROEMULSION

5.1 Introduction

Microemulsions have attracted considerable interest because of their practical applications ever since their introduction (Hoar and Schulman, 1943). One of the definitions of a microemulsion is that it is a thermodynamically stable homogeneous transparent system of low viscosity containing high percentages of both oil and water and, in addition, 15-25 wt % of an emulsifier mixture (Shinoda and Friberg, 1975). The size of a microemulsion droplet is in the range 80-800°A (Schulman et al., 1951). Some of the methods used to determine the size of the droplets are low angle X-ray diffraction (Schulman and Riley, 1948), ultracentrifugation (Bowcott and Schulman, 1955), light scattering (Schulman and Friend, 1949), electron microscopy (Stockenius et al., 1960) and viscosity (Cooke and Schulman, 1965). Many reviews concerning the nature of microemulsions are available in the literature (Bellocq et al., 1984; Prince, 1970; Rosano, 1974; Rosoff, 1978; Shinoda and Friberg, 1975).

The formation and various physicochemical properties of microemulsions are influenced by the alkyl chain length of the surfactant and the cosurfactant as well as the hydrocarbons. For example, the alkyl chain length of alcohol and oil affects the interfacial composition and distribution of alcohol in the oil phase and the aqueous phase of a microemulsion (Bansal et al., 1979; Bansal et al., 1980). In order to examine the structure of the interface of microemulsion droplets, Bowcott and Schulman (1955) titrated water in oil (W/O) emulsions with alcohol as a cosurfactant until a clear microemulsion formed. The amounts of alcohol dissolved in the oil phase and at the interface were determined by plotting the number of moles of alcohol per mole of soap versus the number of moles of oil per mole of soap. The linearity of the titration curve indicates that as the W/O microemulsion is diluted with oil, a constant ratio, K, of alcohol to oil in the external phase (i.e., oil) is required to maintain a clear system (i.e., $K = \frac{n_a^\alpha}{n_o}$). The total number of moles of alcohol in the system, n_a, is given by

$$\begin{aligned} n_a &= n_a^\alpha + n_a^\beta + n_a^\sigma \\ &= n_o K + n_a^\beta + n_a^\sigma \end{aligned}$$

where

n_a^α = number of moles of alcohol in the external phase (oil),

n_a^β = number of moles of alcohol in dispersed phase (water),

n_a^σ = number of moles of alcohol at the interface, and

n_o = number of moles of oil.

Under the assumption

$N_a^\beta << N_a^\sigma$, N_a reduces to

$$N_a = kN_o + N_a^\sigma$$

The intercept of extrapolating the plot of $\frac{n_a}{n_s}$ versus $\frac{n_0}{n_s}$ to zero moles of oil gives the amount of alcohol at the interface. Further, if the surfactant molecules are considered to be present only at the interface, the moles of alcohol at the interface per mole of surfactant can be obtained.

The Schulman-Bowcott model applies mostly for systems that contain long chain alcohols since their solubility in water is negligible.

In the present chapter, the validity of Schulman-Bowcott's model will be examined using a high chain length alcohol, e.g. n-Hexanol.

This model will be used in characterizing mixed hydrocarbons. Finally, the alcohol to oil ratio in the external oil phase of a microemulsion predicted by the Schulman-Bowcott model will be compared with that measured using a fluorescent probe.

5.2 Pyrene Fluorescent Probe

There have been extensive studies on the photophysics of pyrene and its use as a fluorescent probe (Dong and Winnik, 1982; Gratzel and Thomas, 1973; Kim et al., 1981; Lianos et al., 1982; Nakajima, 1971, 1976a,b). The intensities of the various vibronic bands of pyrene were found to show a strong dependence on the solvent environment (Kalyanasundaram and Thomas, 1977; Nakajima, 1971).

In the presence of polar solvents there is an enhancement in the intensity of the 0-0 band at the expense of others due to both the solvent dipole moment and the dielectric constant. The five peaks of pyrene monomer fluorescence in isobutanol and methanol and in isopropanol and dodecane are illustrated in Figures 5.1a,b and 5.2a,b, respectively. In the present study, a linear relationship between the changes in the peak III with respect to the 0-0 band (peak I) and the dielectric constant of a methanol-water mixture is reported. The linear relationship between the ratio of peak III to peak I, hereafter the ratio is referred to as R, and the concentration of one component of a binary mixture holds for several mixtures of alcohols and

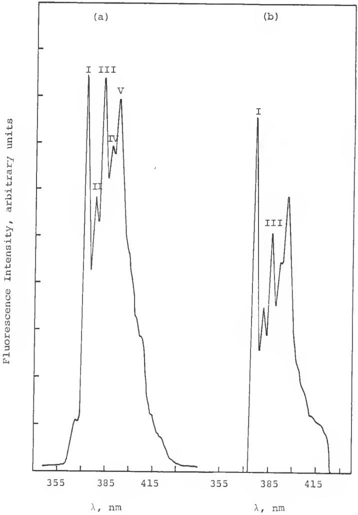

Figure 5.1. Fluroescence Spectra of Pyrene in Isobutanol (a) and Methanol (b).

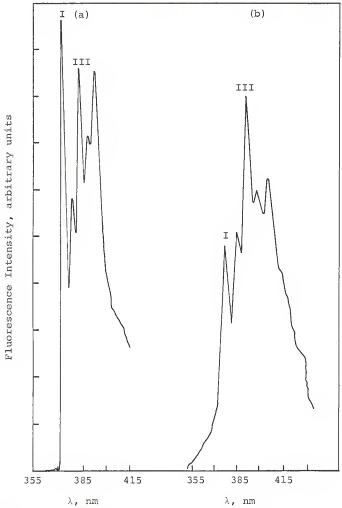

Figure 5.2. Fluorescence spectra of Pyrene in Isopropanol (a) and Dodecane (b).

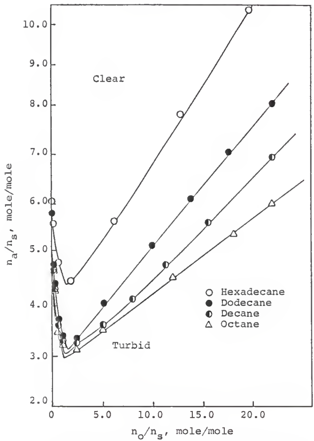

Figure 5.3. Molar Ratios of n-Hexanol to SDS Required to Form Microemulsions in the Presence of Varying Amount of Alkanes at $n_w/n_s = 24.8$.

hydrocarbons. This leads to the estimate of the partitioning of pyrene in the oil phase and the interface of a W/O microemulsion consisting of sodium dodecyl sulfate, n-Hexanol, dodecane and water. Pyrene monomer fluorescence could also be used to determine the alcohol-to-oil ratio in the oil phase of a microemulsion when the volume of the interface is less than 5% of the total volume.

5.3 Experimental

The microemulsions were prepared using sodium dodecyl sulfate (SDS) of 99% purity obtained from BDH chemicals, n-Hexanol of 99% from Sigma, and alkanes of chain lengths 8-16 of purified grade from Fisher Scientific Company. Double distilled water was used in all microemulsion systems. Mixtures of 1:1 molar ratio of hexane and decane, octane and dodecane and octane and hexadecane were also used as the oil phase of the microemulsion. The clear microemulsion was diluted with oil until it became turbid. The turbid emulsion was then titrated with n-Hexanol until it became clear. The dilution data was plotted as total moles of alcohol per mole of surfactant versus moles of oil per mole of surfactant. Several points on the curve near zero moles of oil were determined individually.

The microemulsions used for fluorescent studies were prepared by mixing SDS, water, and dodecane, and titrating with n-Hexanol to get a clear solution. Methanol of spectroscopic grade was obtained from Mallinkrodt Corporation.

Pyrene of 99% purity was obtained from Aldrich Chemical Company.

Fluorescent measurements were carried out on a Perkin Elmer MPF44B spectrophotofluorimeter. The concentration of pyrene in alcohol-water and alcohol-oil mixtures was 1.2×10^{-6} M and in the microemulsion samples 1.03×10^{-5} M. Samples were excited at a wavelength of 331 nm.

5.4 The Influence of Oil Chain Length on Alcohol Partitioning in Various Phases of a Microemulsion

The system chosen for these studies included a molar ratio of water-to-surfactant of 24.8. Figure 5.3 shows a titration curve for the system SDS/hexanol/water/alkane, where n_w/n_s is the ratio of the number of moles of water to the number of moles of surfactant. The plot clearly reveals that a minimum exists below which the amount of alcohol required to yield an optically clear microemulsion increases with a decrease in the alkane content of the system. This observation has also been mentioned for the system potassium oleate-water-benzene-hexanol (Rosoff, 1978). The titration curve for dodecane shown in Figure 5.3 has two distinct regions with respect to its dodecane content, put a narrow region of less than one mole of dodecane in which the number of moles of alcohol in the system increases linearly as the number of moles of dodecane decreases and a broad region above 2.8 moles of dodecane in which the amount of alcohol increases linearly with dodecane.

The same trend was also observed when dodecane was replaced by other alkanes. The structure of these regions is tentatively described as being the same as that proposed by Gillberg et al. (1970).

In the initial region, the system is considered as an inverse micellar hexanol solution. Upon the addition of octane, for example, some of the hexanol molecules originally present in the continuous hexanol phase will be transferred to the interface (Gillberg et al., 1970). This is consistent with the experimental observation that a lesser amount of alcohol is needed as the oil content is increased. The slope of the alcohol-alkane curve in this region provides the number of alcohol molecules that diffuse to the interface for each alkane molecule added to the system. As the oil chain length increases, one hydrocarbon molecule will replace more alcohol in the continuous oil phase. The number of alcohol molecules replaced by one oil molecule increases from 1.37 to 2.31 when octane is replaced by hexadecane.

In the second region, the system is considered as W/O microemulsion with the alkane as the continuous oil phase.

These two distinct regions also clearly emerge when the maximum water solubilization versus the oil concentration of the system at constant alcohol-to-surfactant ratios was measured as shown in Figure 5.4.

As the number of moles of oil is increased initially, the alcohol present in the bulk phase migrates to the

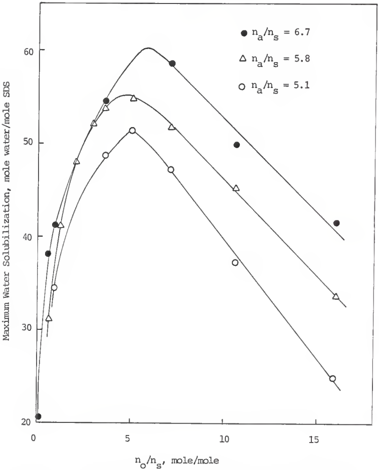

Figure 5.4. Maximum Water Solubilization Versus Various Amounts of Octane at Fixed Ratios of n_a/n_s for the System SDS/n-Hexanol/Water/Octane.

interface and produces additional interfacial area. This increases the solubilization of water in the system. As further oil is added, a stage is reached at which the concentration of alcohol in the bulk oil phase reaches a minimum. Further increase of oil induces the migration of alcohol from the interface to the bulk oil phase to maintain equilibrium between the interface and the bulk oil. This leads to a decrease in the total interfacial area and hence a decreased solubilization capacity. The maximum solubilization of water in oil occurs near $n_o/n_s = 5$ for a fixed concentration of surfactant and alcohol.

Returning to Figure 5.3, the positive slope of each curve represents the number of moles of alcohol per mole of oil. The extrapolation of this portion of the curve to zero oil content gives the number of alcohol molecules per surfactant molecule in the interface of a microemulsion droplet in the W/O microemulsion (Bowcott and Schulman, 1955). The minimum in the alcohol-oil curve represents the minimum amount of alcohol needed to make a microemulsion under the conditions specified. This minimum increases as the oil chain length increases.

Let the negative and positive slopes be referred to as K_1 and K, respectively. Then a plot of K_1 and K versus the equivalent alkane carbon number demonstrates the influence of the oil chain length on these slopes. Furthermore, it will be used as a way of characterizing mixed alkanes. From Figure 5.5, it can be seen that mixed alkanes obey the

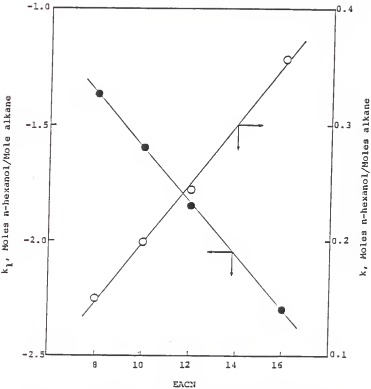

Figure 5.5. Variation of Negative (k_1) and Positive (k) Slopes of Titration Curves with EACN.

equivalent alkane carbon number concept. K_1 varies linearly with the EACN of the oil. The amount of alcohol at the interface of a microemulsion droplet is influenced by the alkyl chain length of alcohol and hydrocarbon (Bansal et al., 1979; Cooke and Schulman, 1965; Sjoblom and Friberg, 1978). The alkyl chain length of alkane is the only variable studied in this section. A further important result obtained from Figure 5.3 is that an increase in the alkyl chain length of the alkane is accompanied by a pronounced increase in hexanol partitioning in both the oil phase and the interface. However, if the data is plotted as concentration of alcohol in the oil phase (in moles/l) versus the oil chain length of alkanes, then only a slight increase in the concentration of alcohol in the oil phase is observed with an increase in the oil chain length as can be seen in Table 5.1 where data of Bansal et al. (1980) is also included. Note that the alcohol-alkane mixture is treated as an ideal solution and the area per molecule for alcohol and SDS are taken as 20°A^2/molecule and 54°A^2/molecule, respectively. As the table shows, the increase in the amount of alcohol in the interface as the oil chain length is increased causes a slight increase in the concentration of alcohol in the oil phase. The increase in the alcohol content of the interface with an increase in alkane chain length may be attributed to the higher interfacial tension between water and alkane. The partition coefficient is taken as the concentration of alcohol in the interface to

Table 5.1. Partitioning of Alcohol in the Interface and Oil Phase of a Microemulsion for the System SDS (1 mole) + Water (24.8 moles) + n-Hexanol + Alkane.

EACN	Moles of Alcohol in Oil Phase/Mole of Alkane	Moles of Alcohol in Interface	Concentration of Alcohol in Oil Phase (mole/1)	Concentration of Alcohol in Interface (mole/cm^2)	Partition Coefficient (cm)
8	0.15	2.62	0.829	4.09×10^{-10}	4.93×10^{-7}
10	0.186	2.68	0.852	4.14×10^{-10}	4.86×10^{-7}
12	0.244	2.75	0.946	4.19×10^{-10}	4.43×10^{-7}
16	0.356	3.42	1.05	4.64×10^{-10}	4.42×10^{-7}
8*	0.14	3.1	0.790	4.44×10^{-10}	5.62×10^{-7}
10*	0.17	3.5	0.797	4.69×10^{-10}	5.88×10^{-7}
12*	0.20	3.6	0.805	4.75×10^{-10}	5.90×10^{-7}
14*	0.28	3.7	0.968	4.80×10^{-10}	4.96×10^{-7}
16*	0.37	3.9	1.111	4.91×10^{-10}	4.42×10^{-7}

*Data of Bansal et al. (1980) where $n_w/n_s = 51$ and n-Pentanol was the alcohol used.

that in the oil phase. The partition coefficient decreases slightly with the EACN which can be attributed to the simplifying assumptions and experimental errors. Hence, the oil molecules should be treated in bulk rather than as individual molecules.

5.5 Surfactant Partitioning in Microemulsion Phases

One of the assumptions made in the estimation of the alcohol per surfactant molecules in the interface of a microemulsion droplet was to neglect any surfactant partitioning in water or oil, i.e., all the surfactant was assumed to be at the interface. An analogous titration experiment is reported here by which surfactant partitioning in the oil and/or water phase of a microemulsion is estimated. In the experiment, a fixed alcohol-to-surfactant ratio and a fixed amount of oil are employed to measure the maximum water solubilization as the surfactant is increased gradually, keeping the alcohol/surfactant ratio constant. In Figure 5.6, the maximum water solubilization versus surfactant weight is shown for a fixed volume of octane and a fixed alcohol-to-surfactant molar ratio of 6.7. The intercept on the surfactant weight axis represents the surfactant amount that is not involved in solubilization of water, i.e., the amount of surfactant not present at the interface. This amount of surfactant is believed to be accompanied by some alcohol in the oil phase. Note that the microemulsions prepared here are all of a W/O type and the

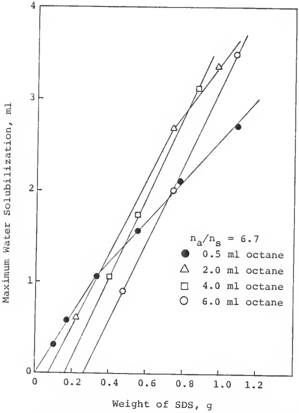

Figure 5.6. Maximum Water Solubilization Versus Surfactant (SDS) Weight at Various Volumes of Octane.

oil phase is octane. From these data, the surfactant solubility in the oil phase can be estimated as shown in Figure 5.7. The solubility of a surfactant in the oil phase decreases as the alcohol-to- surfactant ratio increases because the addition of more alcohol induces a higher alcohol concentration at the interface and therefore more surfactant remains at the interface resulting in a decrease in its partitioning in the oil phase. The slope of each curve shown in Figure 5.7 gives the surfactant partitioning in the oil phase at a particular alcohol to surfactant ratio. For example, at an alcohol-to-surfactant ratio of 5.8, there are approximately 3 surfactant molecules for every 100 octane molecules of the oil phase.

The study presented in this section reveals that appreciable surfactant partitioning in the oil phase is taking place.

5.6 Pyrene Probe

In this section, the result found in the previous sections of this chapter, i.e., the alcohol partitioning in the interface and the oil phase of a microemulsion, will be used to estimate the partitioning of a fluorescent probe, pyrene monomer fluorescence, in the oil phase and the interface of a W/O microemulsion. Consequently, pyrene fluorescence could be used accurately to determine the alcohol-to-oil ratio in the oil phase of a W/O microemulsion

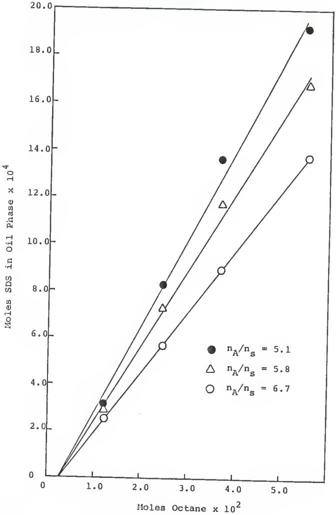

Figure 5.7. Effect of Alcohol-to-Surfactant Ratio on the Number of Moles of SDS in the Octane Phase.

when the volume of microemulsion droplets is less than 5% of total volume.

Pyrene monomer fluorescence in binary mixtures of alcohol and water, and alcohol and alkane was first monitored. For example, pyrene fluorescence in methanol-water mixtures of different methanol concentrations varying from 0%-100% was measured. Figure 5.8 shows that the ratio R of the intensities of peak III to peak I changes linearly with methanol concentration and also with the dielectric constant of the mixture. This behavior of R in binary mixtures of alcohols in water or in hydrocarbon is reproducible.

The microemulsion systems chosen for pyrene fluorescence studies are points just above the clear-opaque line of a Schulman-Bowcott titration curve shown in Figure 5.3 (Bowcott and Schulman, 1955). The number of moles of hexanol in dodecane and at the interface of the microemulsion droplets is calculated respectively from the slope and intercept of the (positive slope) straight line of Figure 5.3, since the solubility of hexanol in water is negligible. The ratio R of hexanol-dodecane mixtures was measured separately as shown in Figure 5.9.

The ratio R of a binary mixture of hexanol and dodecane, which has a concentration identical to that of hexanol in the oil phase of a microemulsion, is 1.51. Table 5.2 reveals that the microemulsion system approaches this value when it is diluted to such a level that the concentration of microemulsion droplets (water + surfactant + alcohol at

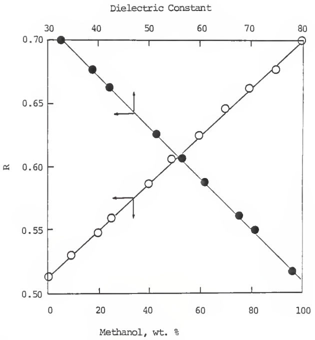

Figure 5.8. Peak III to Peak I Ratio of Pyrene Fluorescence in a Mixture of Methanol and Water. Dielectric constant values are obtained from Janz and Tomkins, 1982.

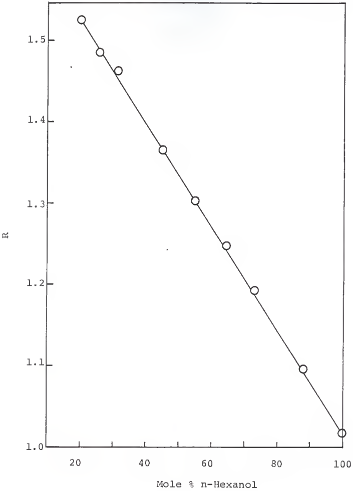

Figure 5.9. Peak III to Peak I Ratio (R) of Pyrene Monomer Fluorescence in a Mixture of n-Hexanol and Dodecane.

interface) is less than 0.05. Another valuable result from the table is that pyrene partitions significantly at the interface of the microemulsion droplets. If a plot of R against the volume fraction of the oil phase (dodecane and n-hexanol in the oil phase) is extrapolated to zero, then a value of R = 1.07 can be taken as that of pyrene fluorescence due to its adsorption at the interface of the microemulsion droplets (Figure 5.10). This value seems to be reasonable because the interface is crowded with hexanol. An empirical relationship of the form

$$R \text{ (microemulsion system)} = \frac{R_o n_o + R_i n_i}{n_o + n_i}$$

can be used to justify the low values of R at high contents of surfactant, water and alcohol in the system, where R_o and n_o are the peak III to peak I ratio and the number of moles of species in the continuous oil phase, respectively; R_i and n_i are the peak III to peak I ratio and the number of moles of species in the interface, respectively. In this relationship, it is assumed that pyrene fluorescence is emitted mainly from its presence in the oil phase and the interface of the microemulsion droplets.

It is to be mentioned that identical studies were conducted on the same microemulsion system by replacing

Table 5.2. The III/I Ratio, R, of Pyrene Fluorescence in a Microemulsion System Containing SDS, Water, n-Hexanol and Dodecane (n_w/n_s=24.8). Microemulsions are on the opaque-clear titration curve.

SDS (gm)	Alcohol (ml)	Dodecane (ml)	R(experimental)	R(calculated)
0.608	1.10	2.43	1.31	1.34
0.526	1.02	2.71	1.34	1.37
0.463	0.96	2.92	1.35	1.39
0.353	0.88	3.27	1.36	1.42
0.313	0.84	3.41	1.41	1.43
0.286	0.82	3.49	1.42	1.44
0.259	0.79	3.59	1.45	1.45
0.186	0.73	3.82	1.46	1.47
0.138	0.69	3.97	1.48	1.48
0.116	0.68	4.04	1.50	1.48

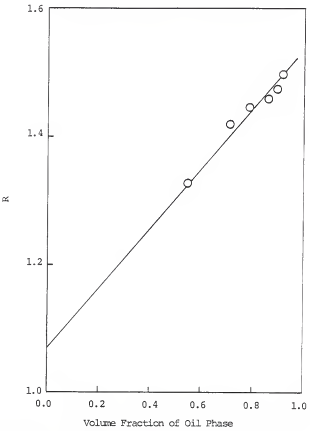

Figure 5.10. Peak III to Peak I Ratio (R) of Pyrene Fluorescence of Water, SDS, Hexanol and Dodecane Microemulsions with $n_w/n_s = 24.8$ at Various Amounts of n-Hexanol and Dodecane. All points are at the clear-turbid titration curve.

n-Pentanol for n-Hexanol and that results similar to those of the system containing n-Hexanol were obtained.

5.7 Summary

The following conclusions are drawn from the results presented in this chapter:

1. The alkane-alcohol opaque-clear titration curve of a surfactant/alcohol/water/alkane system goes through a minimum at a specific alkane content of the system.
2. The microemulsions formed in the two portions of the curve before and after the minimum point may have different structures.
3. The number of n-Hexanol molecules per SDS molecule in the interface of a microemulsion increases with an increase in the alkyl chain length of alkane.
4. Also, the slope of the positive section of the titration curves increases as the alkyl chain length of alkane increases, which indicates an increase in the number of moles of n-Hexanol per mole alkane in the continuous oil phase. This increase is only slight when the calculations are made in a concentration basis because the molar volume of alkanes increases with the alkane carbon number.
5. The titration curves can be used to characterize mixtures of alkanes according to their EACN.
6. Surfactant does partition slightly in the oil phase of a W/O microemulsion.

7. The pyrene monomer fluorescence is quantitatively sensitive to environmental changes of a binary mixture of an alcohol in water and an alcohol in alkanes.
8. Pyrene fluorescence could be used to calculate the alcohol partitioning in the interface and oil phase of a W/O microemulsion.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Equivalent Alkane Carbon Number Concept

The EACN concept has been investigated in various important aspects of enhanced oil recovery. It was concluded that a surfactant of low concentration (0.2% TRS 10-80) reduced the interfacial tension between water and alkanes. This finding was true at a wide range of salinity. The equilibration process was found to be extremely long for some systems.

It was also found that the phase behavior of surfactant systems with a single alkane was identical to that of a mixture of alkanes of the same EACN. In particular, the optimal salinity, the solubilization parameter at optimal salinity, the range or width of salinity of the three-phase region and the phase-separation rates for systems with a single alkane were identical to those with a mixture of alkanes that have the same EACN as that of the single alkane. The analysis of solubilized alkanes by a surfactant formulation showed that the mixture was solubilized as a single component.

When pure and mixed alkanes were employed in surfactant-enhanced oil displacement experiments, the oil displacement efficiency obtained for pure and mixed alkanes (of identical EACN) was the same at the optimal salinity of the surfactant slug

with small variations at other salinities below or above optimal salinity, which might be attributed to in situ alterations of other factors influencing oil displacement such as interfacial tension.

Finally, Schulman-Bowcott titration curves could be used to characterize hydrocarbon mixtures. The slope of the plot of moles of alcohol per surfactant versus moles of oil per surfactant could be used to find the EACN of an unknown mixture of hydrocarbons.

6.2 Surfactant Partitioning in the Aqueous and Oil Phases

The investigation of interfacial tension and surfactant partitioning of a commercial surfactant (at low concentrations) into the aqueous and oil phases reveals that ultralow interfacial tension values are reached only for a specific alkane chain length, i.e., 8. The partitioning of surfactant in the two phases involved can provide very constructive information about the mechanism of lowering the interfacial tension.

More work is needed in this area using commercial and isomerically pure surfactants with the addition of an alcohol which may improve the reproducibility of the surfactant partitioning. The initial surfactant concentration should be selected with great care.

6.3 Criteria of Surfactant Formulations Towards a Good Tertiary Oil Recovery

The lowering of the interfacial tension between oil and water has been singled out by most of the researchers in this field as the most important factor in obtaining high efficiency of oil displacement. But in this work, it is found that other factors may be as important as ultralow interfacial tension.

Surfactant systems containing TRS 10-410/isoamyl alcohol or TRS 10-410/isopropanol blends produced ultralow interfacial tension at their respective optimal salinities, though poor oil displacement efficiency resulted upon using either one of the two blends. The surfactant system that contains isoamyl alcohol forms a middle-phase microemulsion only within very narrow salinity ranges. This state could be altered to an undesired one that contains l- or u-type microemulsions of high interfacial tension upon small *in situ* perturbations in the other factors that influence the salinity range in which three phases occur. On the other hand, the oil displacement efficiency of the surfactant system that contains isopropanol is degraded by the fact that isopropanol is infinitely soluble in water. Consequently, a macroemulsion of surfactant, alcohol, oil and brine forms. This leads to a lack of mobilization of entrapped oil ganglia and hence poor oil displacement efficiency.

Although the studies were performed in sandpacks (high porosity and permeability with low concentrations of multivalent cations), constructive conclusions were obtained. A surfactant formulation with a wide range of three-phase salinity, a rapid rate of coalescence, an ultralow interfacial tension, a large solubilization parameter and an alcohol of low solubility in water, can achieve a successful tertiary oil recovery.

More research in this area is required to confirm the proposed criteria of a surfactant formulation for good tertiary oil recovery. Analogous investigations carried out using a blend of isoamyl alcohol and tert-amyl alcohol with the surfactant could show whether the salinity range of the three-phase region is more important than the solubilization capacity of the surfactant formulation. Moreover, the effect of surfactant loss in the porous medium could be elucidated if some experiments are run in Berea sandstone, which could also reveal more information about the progress of alcohol and surfactant inside the porous medium.

6.4 Phase Behavior of Surfactant Systems

Both the optimal salinity of a surfactant system (5% TRS 10-410 + 3% isobutanol + brine + oil) and the salinity range in which the system forms a middle-phase microemulsion that exists in equilibrium with the excess oil and aqueous phases, increase as the equivalent alkane carbon number of the employed oil is increased. Also, an increase in the EACN results in a decrease in the solubilization parameter at optimal salinity. The rate of separation of the phases

(2 or 3) that form after the surfactant system is left to reach equilibrium is as follows. The rate for the oil phase is very slow at low salinity. Then it increases as the system exhibits three phases reaching a maximum at or close to optimal salinity. Thereafter, an increase in the salinity slows down the rate of separation of the oil phase.

The rate of separation of the brine phase starts slow, and then it accelerates to a maximum value at a salinity slightly more than optimal salinity. Then it becomes slow at high salinities.

The type of alcohol used influences the phase behavior of the surfactant system. In general, both the optimal salinity and the salinity range of the three-phase region decrease as the alkyl chain length of alcohol increases.

6.5 Alcohol Partitioning in the Three Phases of a Single-Phase Microemulsion

The Bowcott-Schulman curve of the number of moles of alcohol (n-Hexanol) per mole of surfactant versus the number of moles of oil (alkanes) per mole of surfactant exhibits a minimum below which the amount of alcohol required to yield a clear solution increases sharply with a decrease in the oil content of the system. The minimum in the curve occurs when the number of moles of oil per mole of surfactant is $\leq$ 2 (depending on the chain length of alkane).

In the absence of alkane, the system is believed to be as an inverse micellar hexanol solution. Upon the addition of alkane, some of the hexanol molecules originally present in the continuous hexanol phase will be driven into the interface and, therefore, less hexanol is needed to make a clear solution. The number of hexanol molecules diffusing to the micellar interface increases as the chain length of alkane is increased.

When alkane molecules dominate the continuous oil phase, the structure is a W/O microemulsion. An increase in the alkyl chain length of alkane is accompanied by an increase in the partitioning of hexanol in both the oil phase and the interface. It is concluded that the estimated partition coefficient (defined as the concentration of hexanol in the interface, in moles cm^{-2}, divided by the concentration of hexanol in the oil phase, in moles cm^{-3}) decreases slightly with an increase in the alkayl chain length of alkane. Following a titration experiment analogous to that of the alcohol-oil titration experiment, the partitioning of surfactant in the oil phase is estimated.

The alcohol-oil titration curve is used to estimate the partitioning of a pyrene fluorescent probe. It is found that pyrene partitions into both the interface and the oil phase of the microemulsion. When the microemulsion droplets occupy $\leq$ 5% of the total volume of the system, pyrene fluorescence can be used to estimate the alcohol/oil ratio of the oil phase. It is also found that a relationship of the form

$$R = \frac{R_o n_o + R_i n_i}{n_i + n_o}$$

can be used to account for the emission of pyrene from its presence in both the interface and the oil phase. In other words, the ratio of the emission intensities of peak III to peak I of pyrene fluorescence from the interface can be estimated.

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BIOGRAPHICAL SKETCH

Faisal Ibrahim Iskanderani was born in 1953 in Medina, Saudi Arabia. He received his precollege schooling at Mahammadeyia Elementary School, Omar bin Al-Khattab Intermediate School and Taiba High School in Medina. He received his B.S. degree in chemical engineering from University of Petroleum and Minerals, Dhahran, Saudi Arabia, in June 1976. He then joined King Abdulaziz University in Jeddah and stayed for a year as a graduate student. He received his M.S. degree in chemical engineering from Stanford Univeristy in June 1979. Subsequently, he continued his work toward the Ph.D. degree in the Department of Chemical Engineering, University of Florida. After graduation, he will return to the Chemical Engineering Department at King Abdulaziz University.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Dinesh O. Shah

Dinesh O. Shah, Chairman
Professor of Chemical
Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Timothy J. Anderson

Timothy J. Anderson
Associate Professor of
Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Dale W. Kirmse

Dale W. Kirmse
Associate Professor of
Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Brij M. Moudgil

Brij M. Moudgil
Associate Professor of
Materials Science and
Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Gerald B. Westermann-Clark

Gerald B. Westermann-Clark
Assistant Professor of
Chemical Engineering

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 1985

Hubert A. Bevis

Dean, College of Engineering

Dean, Graduate School

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